1975

Zirconium Complexes with the 3-Cyanoacetylacetonate Anion: A Potential Trifunctional Ligand

George Arbuthnot Lock
College of William & Mary - Arts & Sciences

ZIRCONIUM COMPLEXES WITH THE 3-CYANOACETYLACETONATE ANION: A POTENTIAL TRIFUNCTIONAL LIGAND

A Thesis

Presented to

The Faculty of the Department of Chemistry

The College of William and Mary in Virginia

In Partial Fulfillment

Of the Requirements for the Degree of

Master of Arts

---

by

George A. Lock, Jr.

1975

APPROVAL SHEET

This thesis is submitted in partial fulfillment of

the requirements for the degree of

Master of Arts

George A. Lock, Jr.
George A. Lock, Jr.

Approved, January 1975

David W. Thompson
David W. Thompson, Ph.D.

Cirila Djordjevic
Cirila Djordjevic, Ph.D.

Trevor B. Hill
Trevor B. Hill, Ph.D.

TABLE OF CONTENTS

ACKNOWLEDGMENTS v

LIST OF TABLES vi

LIST OF FIGURES vii

ABSTRACT ix

Chapter

I. INTRODUCTION 2

3-Cyanoacetylacetone 2

Precedent for Bifunctional Cyanide in Complexes 10

Metal Complexes of 3-Cyanoacetylacetone 19

Zirconium β-Diketonates 25

II. EXPERIMENTAL SECTION 27

Synthesis of 3-Cyanoacetylacetone (3-Cyano-2,4-pentanedione) 27

Synthesis of Cyanobenzoylacetone (2-Cyano-1-phenyl-1,3-butanedione) 29

Synthesis of Cyanodibenzoylmethane (2-Cyano-1,3-diphenyl-1,3-propanedione) 30

Reagents and General Techniques 31

Preparations 31

Synthesis of Dichlorobis(3-cyanoacetylacetonato)zirconium(IV) 31

Synthesis of Chlorotris-(3-cyanoacetylacetonato)zirconium(IV) 37

Chapter

Synthesis of Pentahaptocyclopentadienyltris-(3-cyanoacetylacetonato)zirconium(IV) 38

Synthesis of Dichlorobis-(cyanobenzoylacetonato)zirconium(IV) 39

Synthesis of Tetrakis(3-cyanoacetylacetonato)zirconium(IV) 40

Attempted Preparation of Trichloro-(3-cyanoacetylacetonato)zirconium(IV) 41

Alternate Methods Used in Attempting to Prepare Chlorotris(3-cyanoacetylacetonato)-zirconium(IV) 42

Characterization of Compounds 43

Melting Points 43

Chloride Analysis 43

Zirconium Analysis 44

Carbon, Hydrogen and Nitrogen Analysis 45

Infrared Absorption Spectra 45

Nuclear Magnetic Resonance Spectra 45

III. DISCUSSION AND RESULTS 46

Preparative Chemistry 46

Characterization of the Cyano-β-Diketonate Complexes 52

IV. CONCLUSIONS 77

REFERENCES 78

ACKNOWLEDGMENTS

The writer wishes to express his sincere appreciation to Professor David W. Thompson, under whose direction this investigation was conducted, for his direction and criticism throughout the investigation. The author is also indebted to Professor Cirila Djordjevic and Professor Trevor B. Hill for their careful reading and criticism of the manuscript. Finally, the writer wishes to express a special thanks to his wife, Linda Lock, for her encouragement, assistance, and patience.

LIST OF TABLES

Table		Page
1.	Spectral data for various forms of 3-cyanoacetylacetone and acetylacetone	4
2.	Band frequencies in carbon tetrachloride solution of enol forms of cyanoacetylacetone and d-cyanoacetylacetone and comparison with corresponding frequencies of enol forms of acetylacetone and d-acetylacetone	7
3.	Band frequencies of the free anions of acetylacetone and 3-cyanoacetylacetone in H_2O, D_2O, and KBr	9
4.	Polymeric cyanide complexes	14
5.	Cyanide stretching frequencies of metal complexes of 3-cyanoacetylacetone	21
6.	C-N stretching frequencies observed in cyano-β-diketonate complexes of zirconium(IV)	58
7.	Proton chemical shift data for zirconium-β-diketonate complexes	74

LIST OF FIGURES

Figure		Page
1.	Infrared absorption spectrum of 3-cyanoacetylacetone in carbon tetrachloride	6
2.	Infrared spectrum of deuterated 3-cyanoacetylacetone in carbon tetrachloride solution	6
3.	Spectrum of Na salt of 3-cyanoacetylacetone in KBr in region 1700-800 cm^{-1}	9
4.	Macrocyclic cyanoboranes	13
5.	The structure of μ-bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)dicopper(I)	12
6.	Some cyclic oligomeric cyanides	16
7.	Postulated structure for trichloro-(3-cyanoacetylacetonato)titanium(IV)	24
8.	Preparation of 3-cyanoacetylacetone	28
9.	Diagram of the apparatus for the preparation of the complexes	33
10.	Diagram of the apparatus just before filtration of solid products	34
11.	Diagram of the apparatus just after transfer from reaction flask to filter flask	35
12.	Diagram of the filter funnel when used to dry solid products	36
13.	Infrared spectrum of dichlorobis(3-cyanoacetylacetonato)zirconium(IV) as a mull in Nujol	53
14.	Infrared spectrum of dichlorobis(cyanobenzoylacetonato)zirconium(IV) as a mull in Nujol	54

Figure Page

15. Infrared spectrum of chlorotris(3-cyanoacetylacetonato)zirconium(IV) as a mull in Nujol 55

16. Infrared spectrum of pentahaptocyclopentadienyltris(3-cyanoacetylacetonato)-zirconium(IV) as a mull in Nujol 56

17. Infrared spectrum of tetrakis(3-cyanoacetylacetonato)zirconium(IV) as a mull in Nujol 57

18. The postulated structure of dichlorobis-(3-cyanoacetylacetonato)zirconium(IV) 61

19. The structure of the monomeric unit of chlorotris(3-cyanoacetylacetonato)-zirconium(IV) 63

20. The structure of pentahaptocyclopentadienyltris(3-cyanoacetylacetonato)-zirconium(IV) 65

21. The structure of tetrakis(3-cyanoacetylacetonato)zirconium(IV) 67

22. The methyl proton resonance observed in the nmr spectrum of 3-cyanoacetylacetone 69

23. The methyl proton resonances observed in the nmr spectrum of dichlorobis(3-cyanoacetylacetonato)zirconium(IV) 70

24. The methyl proton resonances observed in the nmr spectrum of chlorotris(3-cyanoacetylacetonato)zirconium(IV) 71

25. The methyl proton resonances observed in the nmr spectrum of pentahaptocyclopentadienyltris(3-cyanoacetylacetonato)-zirconium(IV) 72

26. The methyl proton resonance observed in the nmr spectrum of tetrakis(3-cyanoacetylacetonato)zirconium(IV) 73

ABSTRACT

β-Diketones usually coordinate to metal atoms as the anion *via* both oxygens. Reported herein is the investigation carried out on zirconium complexes of 3-cyanoacetylacetone. Specifically, the existence of a possible third coordinating group, the nitrile, is thought to permit trifunctional bridge bonding with the 3-cyanoacetylacetonate ligand in complexes of zirconium(IV). The properties of 3-cyanoacetylacetone and previously prepared compounds containing cyanide bridges are reviewed. The preparation and characterization of complexes of the type $ZrCl_{4-x}(CAA)_x$ where $x = 2 - 4$, (CAA = 3-cyanoacetylacetonate) and $Zr(h^5\text{-}C_5H_5)(CAA)_3$ received particular attention as did repeated unsuccessful attempts to prepare $ZrCl_3(CAA)$. Efforts to prepare $ZrCl_2(CNbzbz)_2$ and $Zr(CNbzbz)_4$, (CNbzbz = cyanodibenzoylmethanate), and to characterize fully $ZrCl_2(CNbzac)_2$, (CNbzac = cyanobenzoylacetone) were also unsuccessful.

ZIRCONIUM COMPLEXES WITH THE 3-CYANOACETYLACETONATE ANION: A POTENTIAL TRIFUNCTIONAL LIGAND

CHAPTER I

INTRODUCTION

The first synthesis of 3-cyanoacetylacetone (3-cyano-2,4-pentanedione, 2-acetylacetoacetonitrile) was reported in 1898.[1] In contrast to numerous other enolizable β-diketones only a limited amount of work has been undertaken regarding its use as an oxygen-donating bidentate chelating agent in metal complexes.[2,3] While 3-cyanoacetylacetone presents a third donor site through the nitrile group and, thus, is a trifunctional ligand, only one publication exists reporting evidence consistent with trifunctional coordination to metal centers.[4] In this work, the results of the synthesis and the characterization of a series of complexes between zirconium(IV) and 3-cyanoacetylacetone and 2-cyano-1-phenyl-1,3-butanedione are reported.

3-Cyanoacetylacetone

3-Cyanoacetylacetone was initially reported[1] as the hydrolysis product of an intermediate, "cyano-imido-methylacetylacetonate," which was produced by the reaction of cyanogen with acetylacetone. Acetylacetone with a catalytic amount of sodium ethoxide in ethanol reacts with cyanogen (generated from copper sulfate and aqueous sodium cyanide) to form a white crystalline intermediate that decomposes on storage. The imido-intermediate is dissolved in sodium hydroxide solution from which 3-cyanoacetylacetone precipitates as a

white crystalline solid as the solution is brought to pH = 2 with hydrochloric acid.

While this method of preparation seems to be preferred by most of those who have reported on the chemistry of 3-cyanoacetylacetone, studies of its infrared and ultraviolet spectral characteristics have been carried out on the product prepared by an entirely different method.[5] Ultraviolet irradiation (253.7 nm) of 2,6-dimethyl-4-aminopyridine (I) results in an intramolecular rearrangement with the quantitative formation in aqueous or anhydrous media of 2-amino-3-cyanopent-2-ene-4-imine (II). The II is deaminated on heating in aqueous solution to 2-amino-3-cyanopent-2-ene-4-one (III) which in 0.1N sodium hydroxide undergoes further hydrolysis to 3-cyanoacetylacetone.

3-Cyanoacetylacetone is a white crystalline solid which melts at 54 to 55°[2] and sublimes readily. It is a reasonably strong acid[1] with a pK of 3.5 as compared to the enol form of acetylacetone, pK = 8.2.[6] 3-Cyanoacetylacetone exists exclusively in the enol form while acetylacetone is found as a keto-enol (20:80) mixture.[6,7,8] Wierzchowski and Shugar[6] in an investigation of the ultraviolet absorption spectra of 3-cyanoacetylacetone in comparison with that of acetylacetone reported that the shift in tautomeric equilibrium of the former compound completely towards the enol form is due to the electron withdrawing influence of the nitrile group on the third carbon of the pentane skeleton.

It can be seen from Table 1 that the long-wavelength electronic absorption band of 3-cyanoacetyacetone (λ = 280.5 nm) is shifted to a longer wavelength with respect to its corresponding band in the

TABLE 1

SPECTRAL DATA FOR VARIOUS FORMS OF 3-CYANOACETYLACETONE AND ACETYLACETONE

3-Cyanoacetylacetone				Acetylacetone		
Form	Solvent	λ_{max} (nm)	ε	Solvent	λ_{max} (nm)	ε
O-Me ether	aliph. hydrocarbon	232	8000	heptane	242 (*cis*)	12300
(*cis* & *trans*)				heptane	247 (*trans*)	12000
O-Me ether	H_2O	235	7700	methanol	262 (*cis*)	14200
(*cis* & *trans*)				methanol	254 (*trans*)	13500
enol	aliph. hydrocarbon	280, 203	9800, 10100	heptane*	270	10000
enol	H_2O, 0.1N HCl	276, 204	10300, 9400	H_2O, pH≅5.92**	274	1864
enolate anion	H_2O, pH=7	281, 222	1750, 1040	H_2O pH≅10	292	22550

* enol content ≃90%

**enol content ≃25%

spectrum of the enol form of acetylacetone (λ = 270.0 nm). This band is interpreted as a $\pi \longrightarrow \pi^*$ transition of the delocalized system of π-electrons of the intramolecularly hydrogen-bonded cis-enol tautomer. In comparison with the long-wavelength band in the spectrum of the O-Me ether (4-methoxy-3-pentene-2-one), a β-unsaturated ketone, the bands in both enol tautomers are markedly shifted towards lower transition energies pointing to greater delocalization in the enol forms. While the basic structure of the enol tautomers of acetylacetone and 3-cyanoacetylacetone are the same, the electronic effect (inductive and/or resonance) of the nitrile group is the probable cause of a longer wavelength transition relative to acetylacetone. The vibration frequency of the C≡N group in 3-cyanoacetylacetone, 2220 cm^{-1}, is quite close to the frequency of this group in other conjugated nitriles. This is also consistent with the participation of the nitrile group in the delocalized π-system of the intramolecularly hydrogen-bonded enol tautomer.

The infrared absorption spectra of 3-cyanoacetylacetone and d -3-cyanoacetylacetone in CCl_4 solution are presented in Figures 1 and 2. A complete tabulation of the observed bands and their frequencies together with their assignments is presented in Table 2. It can be seen that the main features of the spectra of 3-cyanoacetylacetone are present in the spectra of acetylacetone. In contrast, neither in carbon tetrachloride or acetonitrile solution, nor in the gas phase, is there any sign of 3-cyanoacetyl-acetone absorbing in the region of 1720 cm^{-1} as is expected of the

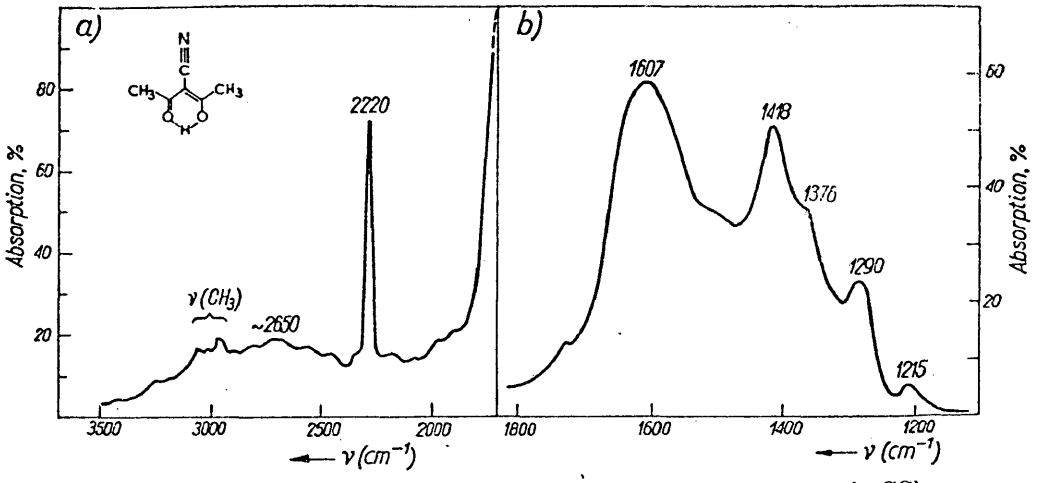


Fig. 1. Infrared absorption spectrum of cyanoacetylacetone in CCl_4:
(a) in region of ν (OH) absorption, ~1·5 M, 0·005 cm.
(b) in region of valence bond stretching frequencies, 0·24 M, 0·005 cm.

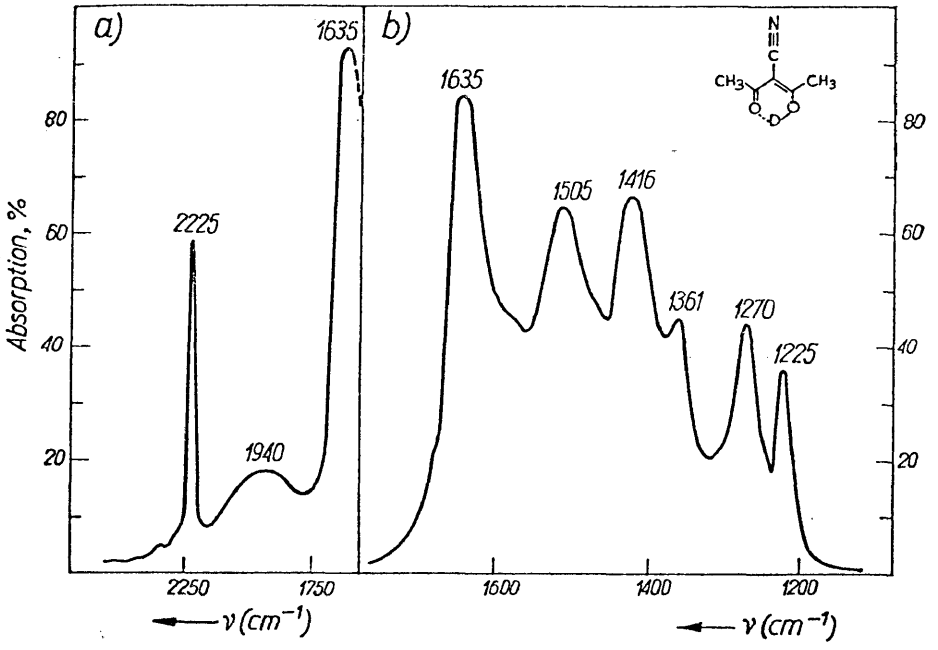


Fig. 2. Infrared spectrum of deuterated cyanoacetylacetone in CCl_4 solution:
(a) in region of ν(OH) adsorption, ~0·25 M, 0·010 cm.
(b) in region 1700–1200 cm^{-1}, ~0·25 M, 0·005 cm.

TABLE 2

Infrared band frequencies (in cm^{-1}) in carbon tetrachloride solution of the enol forms of 3-cyanoacetylacetone and d -3-cyanoacetylacetone and comparison with corresponding frequencies of the enol forms of acetylacetone and d -acetylacetone

$CH_3-C(=O)-C(CN)=C(HO)-CH_3$	$CH_3-C(=O)-C(CN)=C(DO)-CH_3$	Assignment	$CH_3-C(=O)-CH=C(HO)-CH_3$	$CH_3-C(=O)-CH=C(DO)-CH_3$	Assignment
~2650	1940	ν(OH ··· O) ν(OD ··· O)	2700	1980	ν(OH, OD)
2220*	2225	ν(C≡N)	—	—	—
1607‡	1635	$\nu \sim \nu$(C=O)	1616	1621	$\omega \sim \omega$(C=O)†
	1505	$\nu \sim \nu$(C=C)		1536	$\omega \sim \omega$(C=C)
		$\delta(CH_3)_{asym}$	~1450	1425	$\omega \sim \omega$(C—O)
1418	1416	$\nu \sim \nu$C—O)	1419		$\delta(CH_3)_{asym}$
		δ(OH, OD)		1078	δ(OH, OD)
1376	1361	$\delta(CH_3)_{sym}$	1360	1357	$\delta(CH_3)_{sym}$
1290	1270	$\nu \sim \nu$(C—C)	1247	1277	$\omega \sim \omega$(C—C)
1215	1225	$\nu \sim \nu$(C—CN)	—	—	
—	—		1170	1156	$\rho(CH_3)$ (?)
—	—			875	δ(CH, CD) (?)
1022	1024	$\gamma(CH)_3$	1024	1024	$\gamma(CH_3)$
1000	1005		998		
—	—		955	707	γ(OH, OD)
963	984	$\nu(C-CH_3)_{asym}$	—	—	
920	919	$\nu(C-CH_3)_{sym}$	912	936	$\omega(C-CH_3)$
—	—		778	564	γ(CH, CD)
728	712	ring def. (?)	—	—	

* J. P. Fackler (*J. Chem. Soc.* 1957 (1962) reports the same value for ν(C≡N) in $CHCl_3$ solution.

carbonyl group of a ketone; whereas in an acetonitrile solution, about 55% of the acetylacetone is in the keto form. The keto form is clearly detectable in the infrared spectrum by the appearance of two well-defined bands near 1730 cm^{-1} and 1710 cm^{-1} due to the presence of unconjugated C=O group. There is consistent with 3-cyanoacetylacetone existing entirely in the enol form.[9]

However, the resulting -OH group does not show up in the infrared spectrum of 3-cyanoacetylacetone in the 3650 to 3590 cm^{-1} region even in the gas phase at 80°. Instead, there is in carbon tetrachloride solution a very broad, weak band (Figure 1a) centered at 2650 cm^{-1} accompanied by a series of satellite bands; in the deuterated enol (Figure 2a) the 2650 cm^{-1} band is replaced by a band at 1940 cm^{-1}. The absence of a band at 3600 cm^{-1}, the existence of one at 2650 cm^{-1}, and the isotopic shift of this latter band to 1940 cm^{-1} is typical behavior of the stretching frequency for an -OH group involved in a strong hydrogen bond. It can, therefore, be assumed that the enolic -OH must be involved in a strong intramolecular hydrogen bond similar to those encountered in the enol form of acetylacetone and other β-diketones.[10]

Figure 3 exhibits the infrared spectra of the sodium salt of 3-cyanoacetylacetone. (See Table 3.) The anion is assumed to have a symmetrical structure (C_{2v}), i.e., the two C-O bonds are equivalent as are the two C-C bonds in the ring. In passing from the free ligand to the sodium salt of 3-cyanoacetylacetone, the

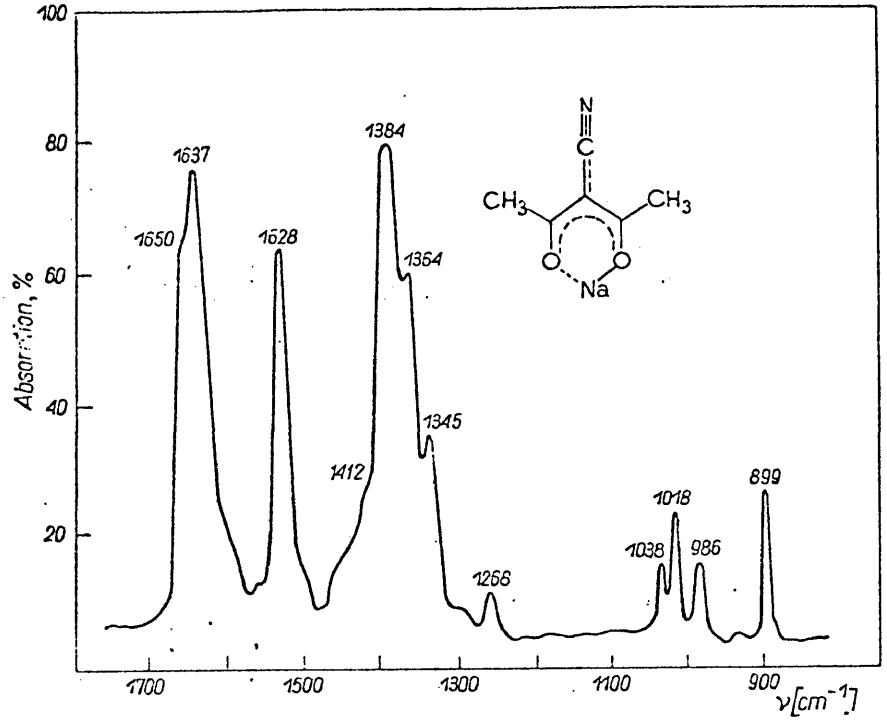


Figure 3

Spectrum of Na salt of 3-cyanoacetylacetone in KBr in region 1700-800 cm^{-1}.

TABLE 3

Band frequencies of the anions of acetylacetone and 3-cyanoacetylacetone in H_2O, D_2O and KBr.

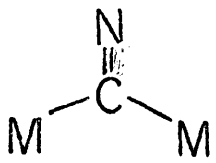
Acetylacetone (Na salt)			Cyanoacetylacetone (Na salt)				Assignment
D_2O	ε_ν[a]	H_2O	D_2O	ε_ν[a]	H_2O	KBr	
—	—	—	—	—	2170	2178	νA_1(—C≡N)
1592	~73	—	1624	~210	—	1650	νB_1(C=C)
1552	—	—	1584	—	—	1637	
1481	~890	1492	1526	~380	—	1528	νB_1(C=O)
1443	—	1443	1424	—	—	1412	$\delta(CH_3)_{asym}$
1417	~530	1423	1390	~440	1380	1384	νA_1(C=O)
1376	—	1372	—	—	—	1364	$\delta(CH_3)_{sym}$
1268	~35	1312	1303	~83	1300	1268	νA_1(C=C)
—	—	—	1349	—	1345	1345	νA_1(C=CN)
1064	—	1185	—	—	1128	1038	$\gamma(CH_3)$
992	—	994	—	—	1046	1018	$\gamma(CH_3)$
962	—	959	1005	—	1021	986	νB_1(C—CH_3)
915	—	—	905	—	936	899	νA_1(C—CH_3)

C-O stretching frequency is decreased from 1607 cm^{-1} to 1528 cm^{-1}. A similar shift is observed for the acetylacetone system. This has been the general observation in the spectra of other metal β-diketonates in which the normal carbonyl modes are replaced by vibrational modes representative of metal coordinated carbonyls.[11] Also noteworthy here is the C-N stretching frequency of the sodium 3-cyanoacetylacetonate at 2170 cm^{-1}.[9] This 50 cm^{-1} decrease from the same vibrational mode of the free ligand has not been interpreted, but a similar frequency shift of 33 cm^{-1} has been reported in the potassium salt.[2]

Nuclear magnetic resonance spectra of acetylacetone and 3-cyanoacetylacetone show -OH peaks at 15.25 ppm and 16.67 ppm (relative to tetramethylsilane), respectively. These low field values are thought to be due to the strong intramolecular hydrogen bonds in these compounds.[7] The larger downfield shift of the enolic proton in 3-cyanoacetylacetone may be due to the electron withdrawing effect of the nitrile group which deshields the proton, or may be related to an increase in the strength of the intramolecular hydrogen bond.

Precedent for Bifunctional Cyanide in Complexes

Although bridging cyanide groups of the type



might be expected by analogy with those formed by carbon monoxide, none have been definitely proved.[12] However, linear bridges are well known and play an important part in the structures of many crystalline cyanide complexes. In fact, cyanide bridges are present in the first recorded synthetic inorganic complex, Prussian blue, $Fe_4[Fe(CN)_6]_3$. (ca. 1700.)

The physical properties of most of the metalloid cyanides suggest that they are polymeric. This polymerization occurs through cyanide bridges. Chaigneau[13] prepared tricyanoborane and reports that the compound melts at 146.5° and is only slightly soluble in organic solvents. In comparison triethylborane, which has a similar molecular weight but does not self-associate, melts at -95° and is exceedingly soluble in organic solvents.

Spielvogel, Bratton, and Moreland,[14] anticipating the instability of monomeric cyanoborane, BH_2CN, predicted that these mixtures could undergo association by formation of coordinate covalent bonds by the donation of a lone pair of electrons of a nitrogen atom into an empty boron orbital. The result of such a process would be the formation of linear and/or cyclic polymers. Some of the oligomeric cyclic molecules which might be expected are depicted in Figure 4. Evidence is reported for a series of macrocyclic oligomers of cyanoborane $(BH_2CN)_n$ with n = 4 - 9.

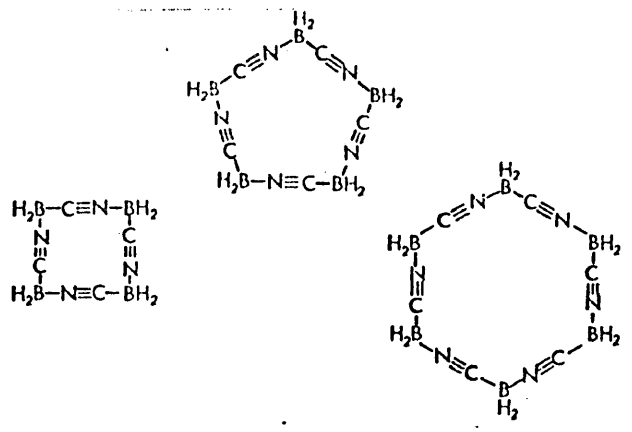


Figure 4
Macrocyclic cyanoboranes

Melmed, Mayerle, and Lippard[15] have determined the structure of μ-bis(cyanotrihydroborato)-tetrakis(triphenylphosphine)-dicopper(I) by single crystal x-ray diffraction study (Figure 5a). The H_3BCN^- ligands bridge two copper atoms forming a ten-membered non-planar ring as illustrated in Figure 5b. Each four-coordinate copper atom is bonded to two triphenylphosphine ligands and to a hydrogen and to a nitrogen atom from different cyanotrihydroborate groups.

Like boron compounds many other metalloidal compounds are potential Lewis acids. Simple cyanides, such as, $Ge(CN)_4$, $As(CN)_3$, $Sb(CN)_3$, and $Bi(CN)_2$, which are insoluble in organic solvents, are, therefore, presumably polymeric.[16] As shown in Table 4, the structures of polymeric transition metal cyanides may involve chains, sheets, or three-dimensional metal-cyanide arrays. Much of the

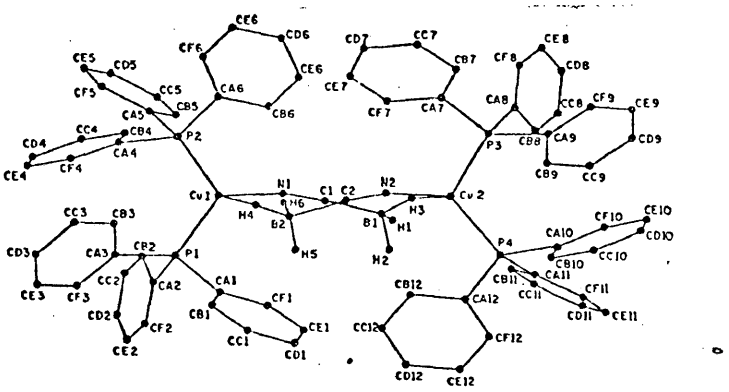


Figure 5a

The structure of
$[((C_6H_5)_3P)_2Cu(NCBH_3)]_2$

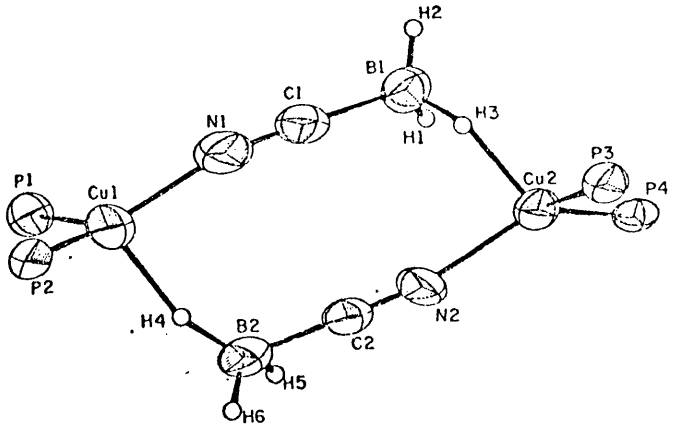
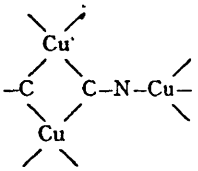


Figure 5b

The ten-membered ring
and its bonded atoms

TABLE 4

Polymeric Cyanide Complexes

Compound	Comments
Chains:	
AgCN	Linear*
AuCN	Linear*
$AgCN \cdot 2AgNO_3$	Approximately linear –Ag–CN–Ag–
$KCu(CN)_2$	Spirals, –Cu–C≡N–Cu–C(=N)–
$CuCN \cdot N_2H_2$	Chains of Cu–C≡N–Cu cross-linked by N_2H_4
Sheets:	
$KCu_2(CN)_3 \cdot H_2O$	Non-linear Cu–C≡N (174 & 176°) Non-linear Cu–N≡C (176 & 152°)
$NiNH_3(CN)_2$	Clathrate compounds may be formed by caging molecules between sheets
$CuCN \cdot NH_3$	 see text
$Ni(CN)_2 \cdot XH_2O$	See text**
$Pd(CN)_2$	See text**
Three dimensional:	
$Zn(CN)_2$	Tetrahedral coord. of metal*
$Cd(CN)_2$	Tetrahedral coord. of metal
$M_xFe^{II}(CN)_6$	Prussian blue analogs*
$M_xFe^{III}(CN)_6$	Prussian blue analogs
$M_xCo^{III}(CN)_6$	Prussian blue analogs
$M_xCr^{III}(CN)_6$	Prussian blue analogs
$M_xRh^{III}(CN)_6$	Prussian blue analogs
$M_xIr^{III}(CN)_6$	Prussian blue analogs
$M_xRu^{II}(CN)_6$	Prussian blue analogs
$M_xMn(CN)_6$	Prussian blue analogs

* CN group was not located with certainty but its position was largely inferred from positions of the heavy atoms.

** Postulated structure

early structural data was collected by x-ray powder techniques which did not afford sufficient information for the exact location of cyanide groups so these were inferred from metal--metal distances (e.g., Prussian blue analogs, $Zn(CN)_2$, $Cd(CN)_2$, AgCN, and AuCN[17]). There is no x-ray evidence for the sheet-like structure of $Ni(CN)_2.H_2O$ and $Pd(CN)_2$; however, this structure is frequently claimed largely on the basis of chemical intuition.[17] In the case of nickel cyanide the sheet-like structure is partially supported by analogy with $Ni(CN)_2.NH_3$ (Figure 6a).[17]

Lewis acids react with cyanide complexes to form simple addition compounds. The reaction of germanium or silicon tetraflouride with dicyanobis(ortho-phenanthroline)iron(III) leads to a variety of cyanide-bridged compounds whose postulated structures are illustrated in Figures 6b and 6c. The cyclic structures were inferred from molecular weight and infrared data.

Stocco, Stocco, Scovell, and Tobias[18] found that dimethylgold cyanide gave osmometric molecular weights which corresponded closely to the tetramer found cryoscopically by Buraway, Gibson, and Holt[19] for the analogous diethyl- and di-n-propyl-compounds. The planar structure for dialkylgold cyanides (Figure 6d) has been suggested on the basis of the original x-ray structure determination of di-n-propylgold cyanide,[20] which located the gold sites as shown, and the methyl proton resonances in the nmr spectrum of dimethylgold cyanide.

Jain,[21] in his study of the coordination compounds between

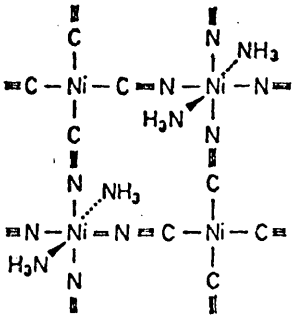


Figure 6a

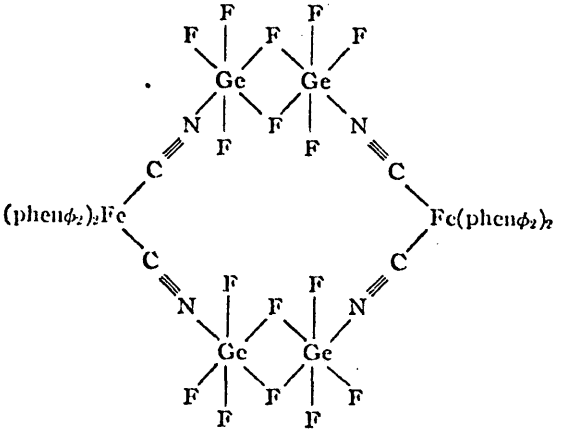


Figure 6b

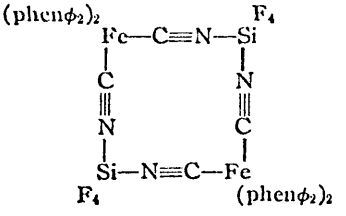


Figure 6c

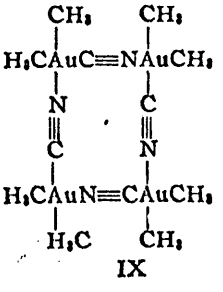


Figure 6d

Figure 6
Some cyclic
oligomeric cyanides

3-cyanopyridine (cypy) and the group (IV) halides, found complexes of the type MX_4.cypy in which infrared spectra suggest coordination through the cyano nitrogen as well as through the pyridine nitrogen. The 3-cyanopyridine molecule has two strong donor groups: the nitrile group and the pyridine group. However, they are sterically prevented from coordinating to the same metal atom. As a bidentate ligand, however, it can coordinate to two different metal atoms. The infrared spectra of known complexes between various metals and nitriles show a marked increase in $\nu(C\equiv N)$ as a result of coordination of the cyano-nitrogen through its free electron pair.[22] The infrared data for the complexes of $TiCl_4$.cypy and $TiBr_4$.cypy as obtained by Jain show that the C-N stretching bands shift to a higher frequency by about 30 cm^{-1} compared to the free ligand. The spectra also retained the characteristics of a coordinated pyridine. These complexes are, therefore, postulated as being hexacoordinate with a bidentate 3-cyanopyridine ligand spanning two metal centers resulting in a polymeric compound.

Jain and Rivest[23] found that the bidentate dicyanoalkanes react with tin(IV), titanium(IV), and zirconium(IV) to give complexes of the type $(MX_4)_2L$, MX_4L or MX_4L_2 where $L = N\equiv C\{CH_2\}_nC\equiv N$, depending upon the reaction conditions and the alkyl cyanide used. Although few structural studies were carried out on these complexes, the $(MX_4)_2L$ and MX_4L adducts are believed to be polymeric. The presence of free and coordinated cyanide groups was inferred from the infrared spectra of the MX_4L_2 adducts. It was concluded that

these complexes are six-coordinate addition compounds with only one nitrile group of each alkyl cyanide molecule coordinated.

Kubota and Schulze[24] have also prepared several 1:1 adducts with dicyanoalkanes and tin(IV) and titanium(IV) chloride, which they suggested were polymers with cyanide bridging.

Farona and Kraus[25] prepared the compounds $M(CO)_3(NCRCN)X$ ($M = Mn,Re$; $X = Cl,Br$; $R = -CH_2-$, $-CH_2CH_2-$, $-CH_2CH_2CH_2-$, ortho $-C_6H_4$) and $M(CO)_3(CH_3CN)_2X$. Whereas the acetonitrile derivatives coordinate in the usual manner through the lone pair of electrons on the nitrogen and exhibit the characteristic increase in the C≡N stretching frequency upon coordination, the dinitriles all show large "decreases" in their CN stretching frequencies and, therefore, appear to be coordinated as bidentates through their C≡N triple bonds.

The observed decrease in C≡N stretching frequency is a result of the coordination of the triple bond to the metal. When this occurs, one of the metal orbitals is able to overlap with the bonding molecular orbitals of the nitrile group to give a sigma bond, while another can interact with the empty anti-bonding molecular orbitals of the ligand which results in a pi-type bond. Thus, the transfer of electrons from the nitrile group of the ligand to the metal in the formation of a sigma bond can probably be enhanced by the simultaneous removal of electrons from the metal through pi back-donation to the ligand.

Both removal of electrons from the bonding orbitals of the C≡N triple bond, and donation into its pi-antibonding orbital will

tend to weaken and lengthen the C-N bond. In accordance with a longer, weaker bond, a decrease in the C-N stretching frequency is usually expected in nitriles coordinated to transition metals through pi-bonding.

As pointed out earlier, cyanides can coordinate to metal halides via the lone pair of electrons on the nitrogen atom. The fact that coordination takes place through the nitrogen atom and not through the triple bond of the nitrile group is indicated by infrared analysis. In many of the nitrogen sigma-bonded compounds discussed an increase in the C-N stretching frequency has been observed.

In conclusion, analysis of literature reports of complexes containing the cyanide ion or dicyanoalkanes shows that complexes whose empirical formula renders the metal coordinatively unsaturated most often have polymeric structures with bridging cyanide groups such that the metal achieves its normal coordination number. Examples range from the oligomeric cyanoboranes to the transition metal alkylcyanides and 3-cyanopyridine complexes. Finally, the infrared frequency shift characteristic of bifunctional cyanides has been shown to provide a good diagnostic tool when cyanide bridges are suspected.

Metal Complexes of 3-Cyanoacetylacetone

As has been mentioned, 3-cyanoacetylacetone is a moderately strong acid and the enolic proton is easily lost to give the enolate anion. As with β-diketonate anions, in general, numerous derivatives

of this anion can be postulated giving rise to a variety of metal-ligand bonding structures. In addition to the general structures of β-diketonate complexes, the 3-cyanoacetylacetonate anion is a trifunctional Lewis base and can coordinate in principle to acceptor sites through both oxygens and the nitrogen.

The most frequently occurring β-diketonate derivatives are those in which the enolate anion is coordinated to a central metal atom through both oxygen atoms. Several studies have provided evidence concerning the structure of the chelate ring.[26] An x-ray crystallographic study of tris(acetylacetonato)iron(III) by Roof,[27] in which interatomic distances were established to within ±0.02Å, is particularly important. Roof's results led to the following conclusions:

1. the six-membered ring is essentially planar;
2. the individual rings have C_{2v} symmetry, i.e.,

the pairs of Fe-O, O-C, and C-C bonds are of equal length to within experimental error; and

3. the ring C-C distances are 1.39Å, intermediate between single and double bond distances (and also equal to the C-C distance in benzene), and the C-O distances are 1.28Å, also intermediate between single and double bonds.

Fackler[2] prepared twelve metal complexes of 3-cyanoacetylacetone and measured the infrared stretching frequencies of their nitrile groups (see Table 5). Since the nitrile group is conjugated with the chelate ring in metal complexes of this ketone, the frequency shift of the infrared cyanide band relative to the free

TABLE 5

Cyanide stretching frequencies of metal complexes of 3-cyanoacetylacetone (L=3-cyanoacetylacetonate anion)

Complex	Solvent	ν_{max} (cm^{-1})
FeL_3	$CHCl_3$	2216.0
CrL_3	$CHCl_3$	2216.3
CoL_3	$CHCl_3$	2216.6
AlL_3	$CHCl_3$	2217.2
GaL_3	$CHCl_3$	2217.5
InL_3	$CHCl_3$	2215.4
BeL_2	$CHCl_3$	2220.5
	KBr	2218.7
CuL_2	$CHCl_3$	2212.5
	KBr	2196.2
ThL_4	$CHCl_3$	2211.6
	KBr	2211.9
ZnL_2	KBr	2225.4

3-cyanoacetylacetone might give some indication concerning the extent of the interaction between the metal ion pi-type orbitals and the ligand pi-system. The overall effect on the C-N stretching frequency produced by formation of these metal complexes is small. This suggests that the interaction of the metal orbitals with the pi-electrons of the chelate ring in the complexes is not extensive. However, some mixing of the ligand and metal pi-orbitals is thought to occur when symmetry permits.[2,26]

Lewis and Nyholm[3] prepared tris-3-cyanoacetylacetonatotitanium(III) as part of a study of a series of tris-β-diketonatotitanium(III) complexes. They found that tris-3-cyanoacetylacetonatotitanium(III) is a monomeric nonelectrolyte in nitrobenzene solution. The visible spectrum of the purple complex in benzene solution consists of an intense band at 17,300 cm^{-1} with shoulders (attributed to vibrational fine structure) at 16,130; 18,520; and 20,830 cm^{-1}. The intense band is thought to be due to a "d-d" transition.

Thompson, Barrett, Lefelhocz, and Lock[4] have reported the preparation of trichloro(3-cyanoacetylacetonato)titanium(IV), Cl_3TiL, and trichloro(3-cyanoacetylacetonato)tin(IV), Cl_3SnL. Evidence is presented which suggests that these complexes are oligomeric and that bridging is accomplished by a novel interaction involving the planar trifunctional 3-cyanoacetylacetonate anion. The infrared spectra of these complexes indicate typical β-diketonate-metal complexes in which the ligand is chelated to the metal center through the oxygen atoms. Noteworthy is the fact that

for Cl_3TiL, the C-N stretching frequency is observed at 2242 cm^{-1}, and for Cl_3SnL at 2234 cm^{-1}, whereas Fackler[2] reported metal complexes of 3-cyanoacetylacetone as having C-N stretching frequencies generally at 2220 cm^{-1}. This observed increase in stretching frequency is interpreted as being due to the interaction of the nitrile group of an oxygen chelated ligand with the metal center of a second Cl_3ML monomeric unit. The absence of prominent infrared bands at 200 to 300 cm^{-1}, the region for bridging Ti-Cl stretching modes, supports the claim that Cl_3TiL differs structurally from trichloroacetylacetonatotitanium(IV) which is a chloride bridged dimer, and that the sixth coordination site of the octahedron is filled by means of the planar trifunctional bridging of the 3-cyanoacetylacetonate ligand coordinated to an adjacent metal center. A symmetric cyclic tetrameric structure rather than an open structure is suggested for the Cl_3ML complexes on the basis of the observed single, shifted, infrared cyanide band. The absence of an uncoordinated C-N band at 2220 cm^{-1} is not consistent with the possibility of an open structure except perhaps in the case of a macromolecular species, which is thought to be unlikely in this type of compound. A cyclic tetramer, as shown in Figure 7, can be formed without distorting the octahedral-like symmetry of the component monomer units and without disturbing the planarity of the chelate ring. Precedent for cyano-bridged cyclic oligomers exists

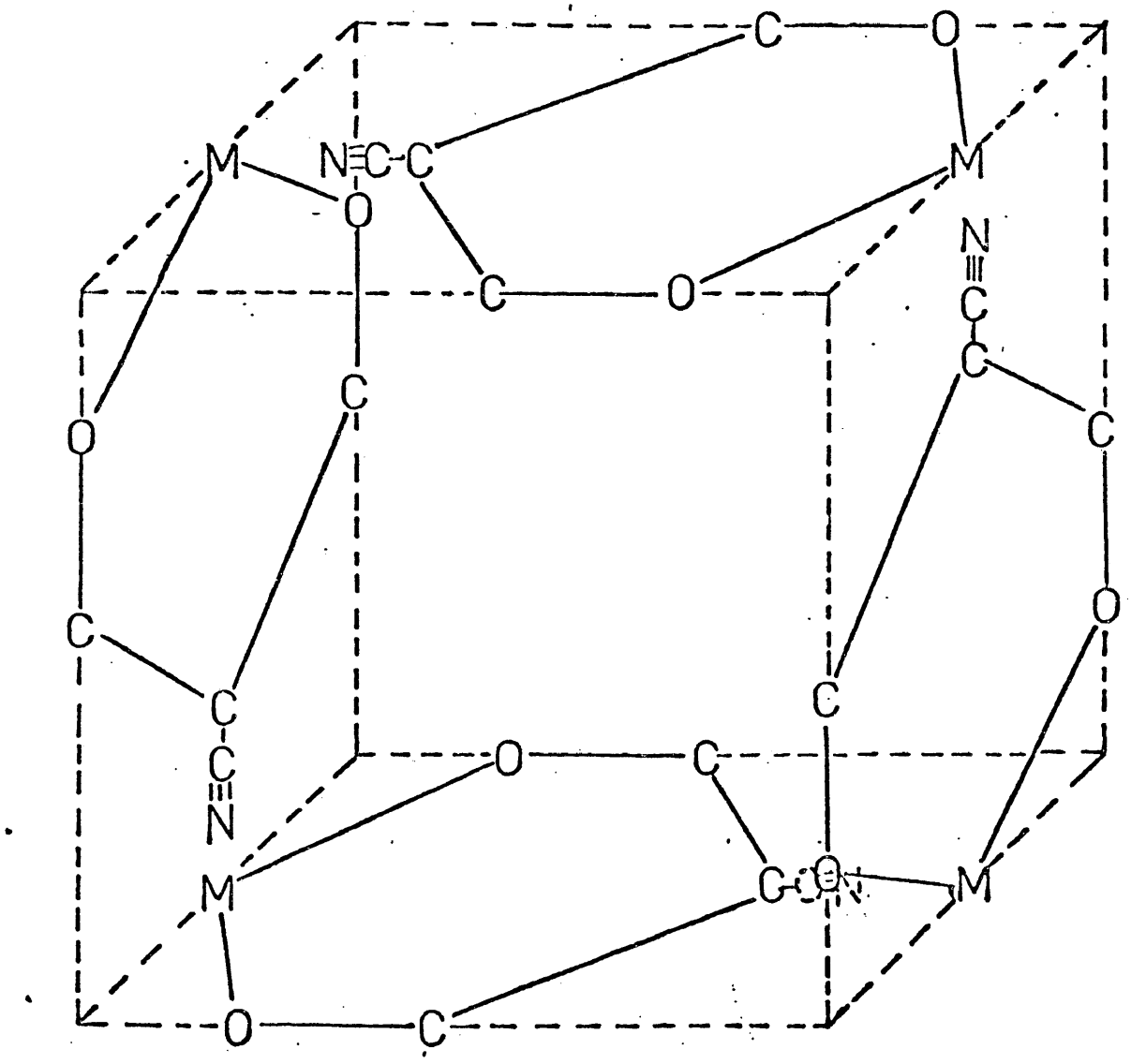


Figure 7

Postulated structure of

trichloro(3-cyanoacetylacetonato)titanium(IV)

in the dialkylgold cyanides[18] and the 1:1 adduct formed between dicyanobis(o-phenanthroline)iron(III) and germanium and silicon tetrafluorides[17] presented earlier.

Zirconium β-Diketonates

Although β-diketonates are known for many metals, zirconium is unique in that it is the only non-radioactive element which has been reported to form β-diketonates in which the metal may exhibit coordination numbers of six, seven, and eight.[28] In the series $Zr(diketo)_2X_2$, $Zr(diketo)_3X$, and $Zr(diketo)_4$, the dihalides are reported as monomeric weak electrolytes in solution,[28] and are generally assumed to contain a six-coordinate metal center. Proton chemical shift data[28] and infrared and Raman spectra[11] indicate that the dihalides exist in solution as the cis-geometric isomer. After a period of some controversy, the monohalides now seem to be thought of as seven-coordinate based on molecular weight measurements,[29] conductance data,[29] and proton magnetic resonance spectra.[28] The tetrakis-β-diketonate complexes are eight-coordinate, usually with a square anti-prismatic structure.

Pentahaptocyclopentadienylzirconium-β-diketonates of the type $Zr(h^5\text{-}C_5H_5)(diketonate)_3$ and $ZrCl(h^5\text{-}C_5H_5)(diketonate)_2$ have also been prepared.[30,31] As before, these compounds are thought to be seven- and six-coordinate, respectively. Molecular weight and conductivity data indicate that these complexes are monomeric weak electrolytes in solution. Bidentate coordination of the ligands has been verified by nmr and infrared spectral data. Apparently,

substitution of a pi-bonded cyclopentadienyl ring for a halide does not appear to affect the mode of bonding of the β-diketonate ligands in these complexes.

Against this background, it was thought that the 3-cyanoacetylacetonate anion might act as a trifunctional ligand in forming complexes with zirconium tetrachloride and dichlorobis-cyclopentadienylzirconium(IV). Attempts to make and characterize a series of such substitution products are discussed.

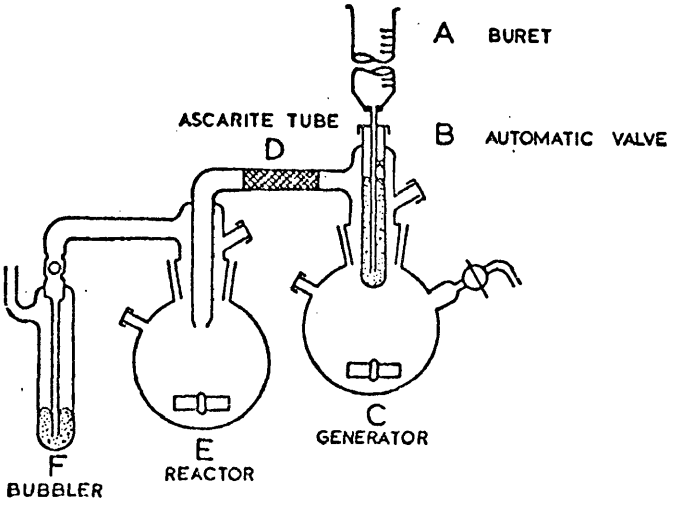
CHAPTER II

EXPERIMENTAL SECTION

Synthesis of 3-Cyanoacetylacetone (3-Cyano-2,4-pentanedione)

Approximately 0.5g of sodium metal was dissolved in 100 ml of cold absolute ethanol (U.S. Industrial Chemicals Co., U.S.P.) in the reactor vessel E. (See Figure 8.) Acetylacetone (Aldrich Chemical Co.; 25.0 ml, 243 mmol) was added to the vessel and it was attached to the apparatus and surrounded by an ice-water bath. Sodium cyanide (Fisher Scientific Co., reagent grade) solution (250 ml, 4 molar) was added dropwise from buret A through the automatic mercury valve B onto a slurry of copper sulfate pentahydrate (Fisher Scientific Co., technical grade; 156g, 625 mmol) in 100 ml of water in the generator flask C in a room temperature water bath. Sodium cyanide solution (50 ml, 5.71 molar) was injected through the side-arm of valve B while stirring was halted in flask E. When generation of cyanogen was complete, as evidenced by the cessation of bubbles escaping through the mercury bubbler F, stirring was resumed in flask E. The uptake of cyanogen was observed as the pressure within the system decreased as indicated by the rising mercury column in F. The stopcock (not shown) on buret A was opened, and sodium cyanide was admitted to the generator C as cyanogen was consumed in E.

$$2\ CuSO_4 + 4\ NaCN \longrightarrow (CN)_2 + 2\ CuCN + 2\ Na_2SO_4$$



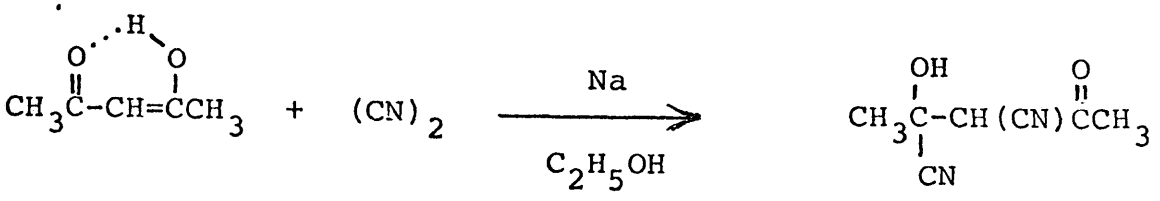


Figure 8
Preparation of 3-cyanoacetylacetone

After the uptake of cyanogen appeared to be complete, the solid reaction intermediate was filtered from the reaction solution and washed with cold absolute ethanol. The white solid was dissolved in 200 ml of 3N NaOH solution. The aqueous solution was cooled in an ice-water bath and brought to pH = 2 with 6N HCl solution whereupon the formation of white crystals (3-cyanoacetylacetone) was observed. The crystals were filtered, washed with cold 1N HCl solution, dissolved in 50 to 60 ml of dichloromethane and dried over anhydrous magnesium sulfate. The filtered organic solution was pulled to dryness under reduced pressure at approximately 40° C. The solid product was sublimed under vacuum at approximately 40° C to give fine, white, needle crystals. A maximum yield of 38%, based on acetylacetone, was obtained. M.p. 52.5 - 54.0°, lit. 50°[1]; $\nu(C\equiv N)$ = 2219 cm^{-1} (relative to the CO_2 peaks at 2367 and 2336 cm^{-1}); δ_{-OH} = 16.59 ppm, δ_{CH_3} = 2.42 ppm.

Synthesis of Cyanobenzoylacetone
(2-Cyano-1-phenyl-1, 3-butanedione)

This compound was prepared and purified by the same procedure as that described for 3-cyanoacetylacetone. However, the benzoylacetone (Eastman Kodak Co.) (12.5g, 77.1 mmol) is a solid at room temperature and was dissolved in 25 ml of benzene before addition to the sodium/ethanol mixture in flask E. All other reagents and solvents were used at 0.33 of their previous quantity with the exception of the sodium cyanide solution injected initially to purge the apparatus--the same amount of solution was used here.

Since no solid intermediate was obtained, the 3N NaOH solution was added directly to the reaction solution and the mixture was brought to pH = 2 with 6N HCl. The crude product that formed was filtered, as before, dissolved in 150 ml of ethanol at 80°, and recrystallized with 100 ml of cold water. The white crystals were dried in dichloromethane over anhydrous magnesium sulfate and sublimed. A yield of 22%, based on benzoylacetone, was obtained. M.p. 71-73°. Anal. Calcd. for $C_{11}H_9O_2N$: C, 70.58; H, 4.85. Found: C, 71.51; H, 4.80. $\nu(C\equiv N)$ = 2221 cm^{-1} (relative to the CO_2 peaks at 2367 and 2336 cm^{-1}); δOH = 17.44 ppm; δ CH_3 = 2.47 ppm.

Synthesis of Cyanodibenzoylmethane (2-Cyano-1,3-diphenyl-1,3-propanedione)

This compound was prepared and purified by the same procedure as that described for 3-cyanacetylacetone. However, the dibenzoylmethane (Eastman Kodak Co.) (23.12g, 103.1 mmol) is a solid at room temperature and was dissolved in 75 ml of benzene before addition to the sodium/ethanol mixture in flask E. All other reagents were used at 0.5 of their previous quantity with the exception of the sodium cyanide solution injected initially to purge the apparatus--the same amount of solution was used here. The white crystals were dried in dichloromethane over anhydrous magnesium sulfate, the solid was stripped of dichloromethane and dried in vacuo at room temperature for several hours. A yield of 10%, based on dibenzoylmethane, was obtained. M.p. 157-159°. Anal. Calcd for $C_{16}H_{11}O_2N$: C, 77.09; H, 4.46. Found: C, 77.02; H, 4.48.

$\nu(C\equiv N)$ = 2221 cm^{-1} (relative to the CO_2 peaks at 2367 and 2336 cm^{-1}); δ_{OH} = 18.03 ppm.

Reagents and General Techniques

Anhydrous zirconium tetrachloride (Alfa Products, Inc.) and anhydrous dichlorobiscyclopentadienylzirconium(IV) (Apache Chemical Co.) were used as purchased. All solvents used were better grades. Benzene (Fisher Scientific Co., B-245) and hexane (Fisher Scientific Co., H-291) were dried by distillation from calcium hydride (Fisher Scientific Co., C-94); dichloromethane (Fisher Scientific Co., D-37) from phosphorous pentoxide (Fisher Scientific Co., A-245); and triethylamine (Eastman Kodak Co., 616) from barium oxide (Baker and Adamson, 1422). All were stored under dry nitrogen over molecular seives (Linde 4-A).

All operations involved in the synthesis of the metal complexes were conducted under anhydrous conditions (dry nitrogen and/or vacuum) in glassware patterned after Kontes Glass Company Airless Ware[32] designed by Shriver.[33] Samples for analysis (elemental, m.p., infrared, nmr) were handled in a Vacuum Atmospheres Dri-Lab[34] under dry nitrogen.

Preparations

Synthesis of Dichlorobis(3-cyanoacetylacetonato)zirconium(IV)

The reaction to prepare this complex was carried out in a 100 ml three-necked round bottom flask equipped with a magnetic

stirrer, a nitrogen inlet, and a dropping funnel which was replaced during the course of the experiment by a reflux condenser (see Figure 9). The apparatus was flamed under nitrogen and allowed to cool before the addition of reactants. All liquids were transferred in syringes. 3-Cyanoacetylacetone (4.26g, 34.0 mmol), dissolved in 25 ml of dichloromethane was added dropwise from the dropping funnel to anhydrous zirconium tetrachloride (7.94g, 34.1 mmol) in 50 ml of dichloromethane in the round bottom flask at 0° with stirring. At the completion of addition, the dropping funnel was replaced with a reflux condenser topped with a nitrogen inlet. The original nitrogen inlet was closed and the reaction mixture was refluxed for 1.5 hours. The white solid remaining after reflux was filtered under nitrogen using the apparatus shown in Figures 10 and 11.

The cloudy filtrate was reduced in volume with mild heat under reduced pressure. There were 50 ml of hexane added, whereupon a large amount of white solid precipitated. The volume of the mixture was further reduced to approximately 50 ml. The product was filtered as before and dried <u>in vacuo</u> at room temperature in the funnel as shown in Figure 12 for several hours. M.p. 236-238° with some prior decomposition. <u>Anal</u>. Calcd for $ZrCl_2(C_6H_6O_2N)_2$: C, 35.12; H, 2.95; Cl, 17.28; Zr, 22.23. Found: C, 34.78; H, 3.31; Cl, 17.24; Zr, 22.40. Λ_M($8X10^{-3}$M soln in CH_3CN) = 14 mhos-mol^{-1}.

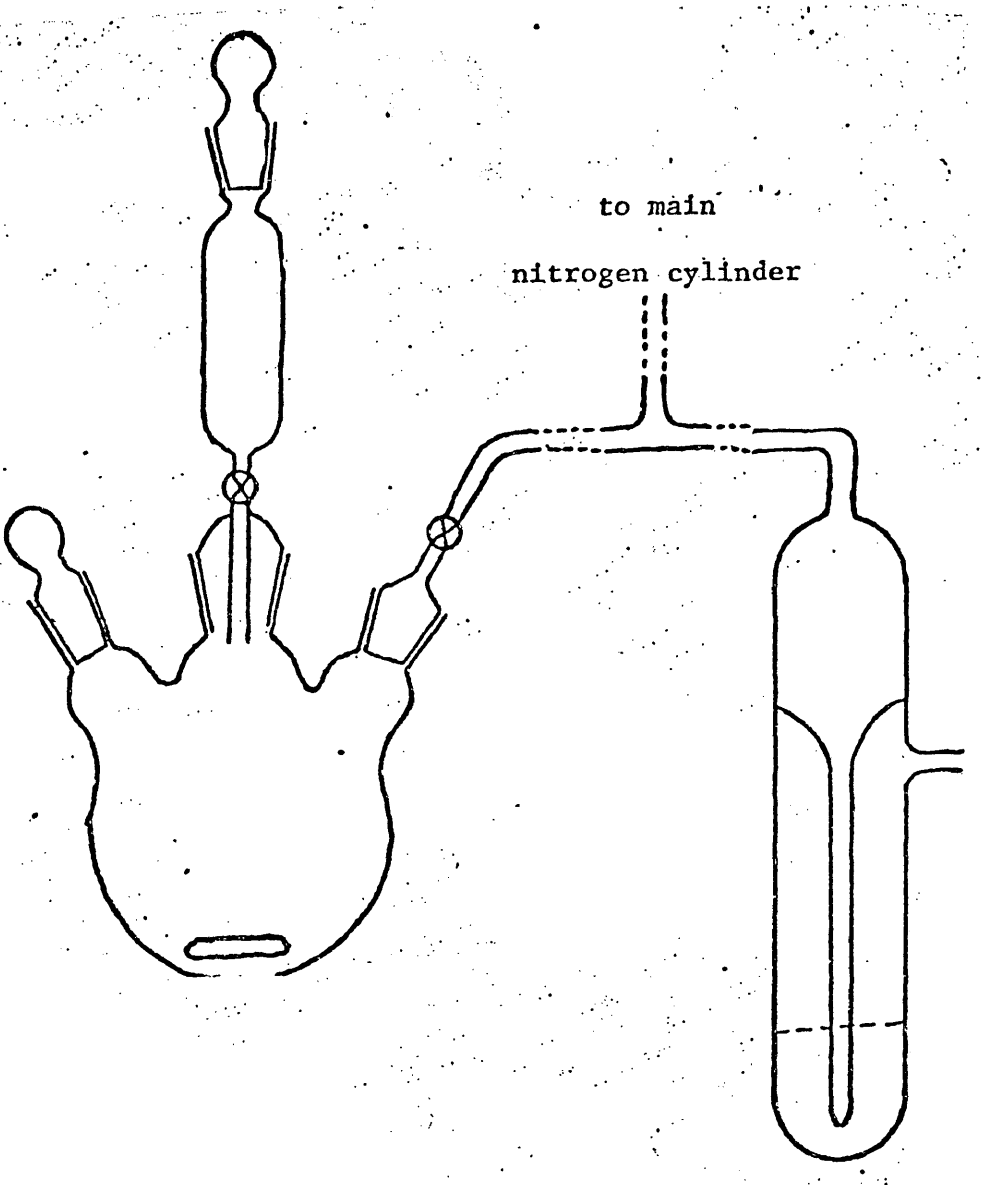


Figure 9

Diagram of the apparatus for the preparation of the zirconium complexes

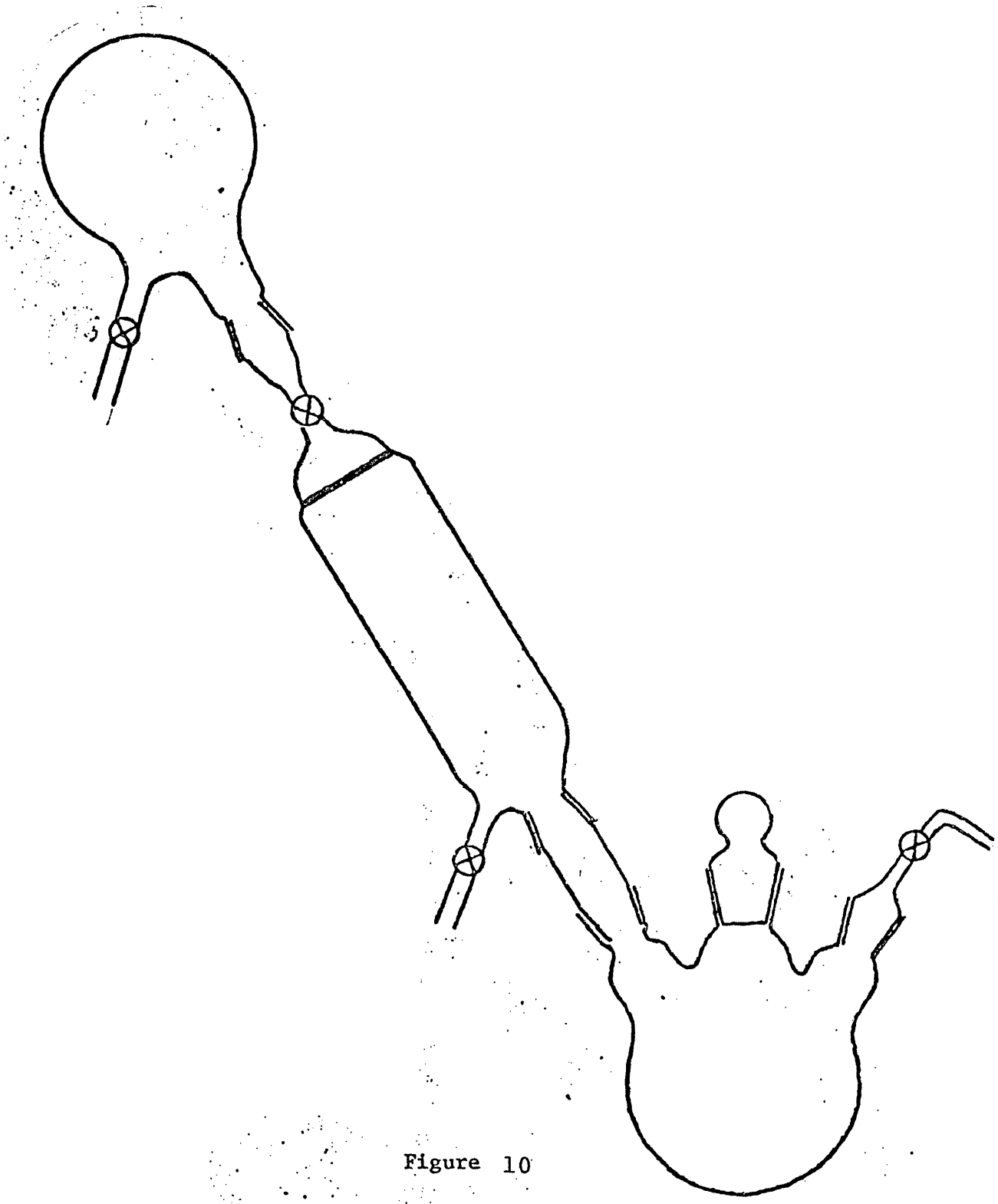


Figure 10

Diagram of apparatus just before filtration of solid products

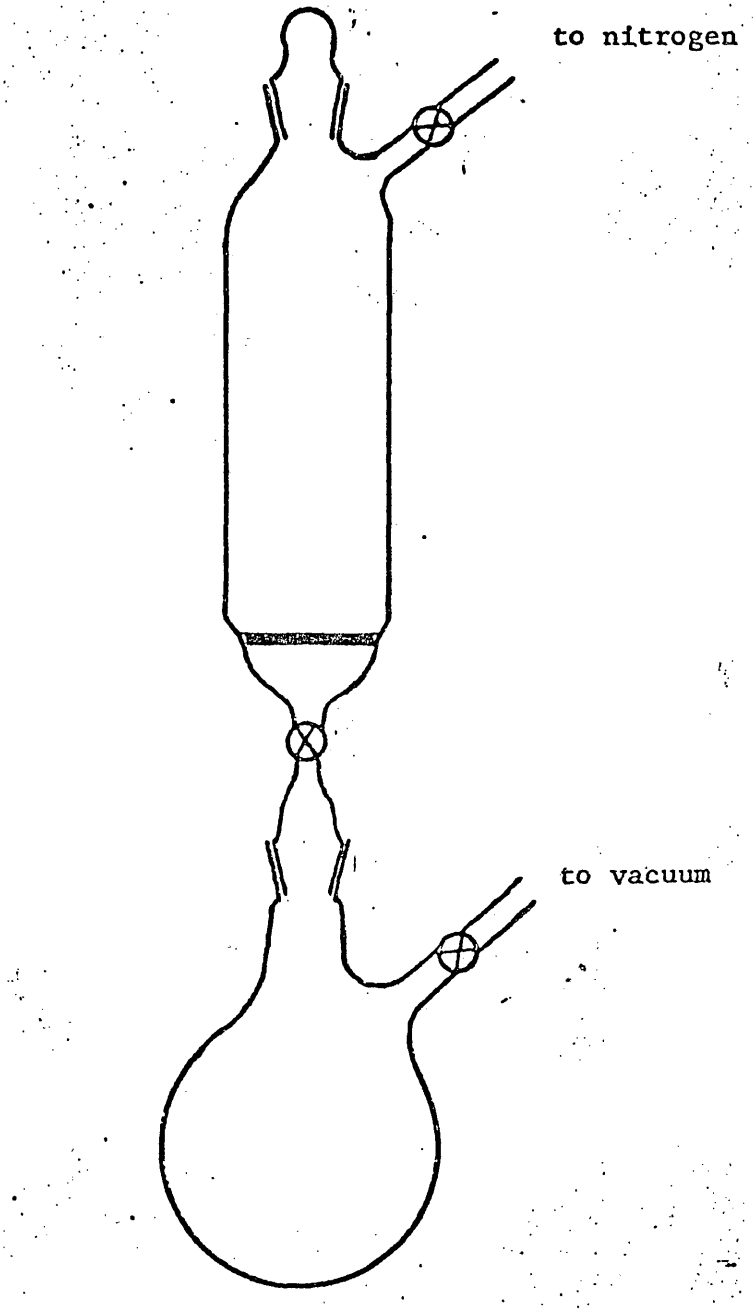


Figure 11

Diagram of apparatus just after transfer from reaction flask to filter flask

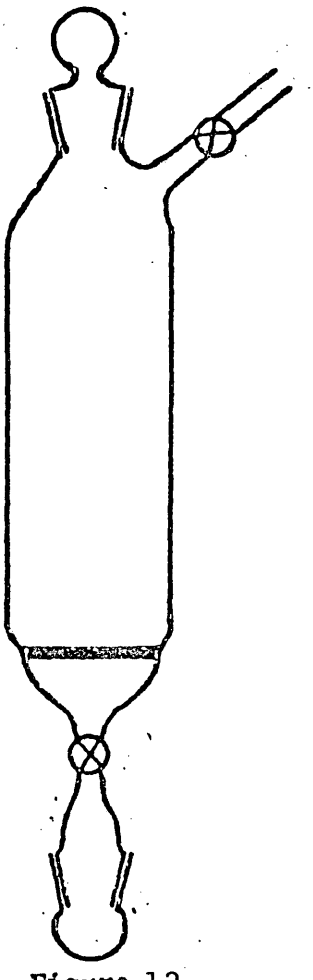


Figure 12

Diagram of the filter funnel when used to dry solid products

Synthesis of Chlorotris-
(3-cyanoacetylacetonato)-
zirconium(IV)

Apparatus and techniques used in the synthesis of this product were similar to those used in the previous synthesis.

3-Cyanoacetylacetone (3.03g, 24.2 mmol), dissolved in 25 ml of dichloromethane, was added dropwise to anhydrous zirconium tetrachloride (3.14g, 13.5 mmol) in 50 ml of dichloromethane at 0°. At the completion of addition, the reaction mixture was refluxed for three hours. The solid remaining after reflux was filtered under dry nitrogen as before. The cloudy filtrate was sealed under dry nitrogen and stored overnight at 5°.

Precipitates that were formed after overnight storage were filtered as before and dried in vacuo at room temperature for several hours. M.p. decomposed from 195° to 240°. Anal. Found: Cl, 22.26.

After standing for several hours at room temperature, the second filtrate had precipitated more solids. This filtrate was pulled to dryness with mild heat under reduced pressure and the solids were resuspended with a 1:1 solvent mixture of dichloromethane and hexane. The solids were filtered as before, washed with 5 ml of hexane, and dried in vacuo at room temperature for several hours. M.p. 234-238° with some prior decomposition. Anal. Found: Cl, 16.16. (The disubstituted product [see previous synthesis] should have a chloride analysis of 17.28%. This solid is probably predominantly the dichloride with a small amount of the monochloride present.)

The filtrate from the isolation of the previous solid was heavily suspended with white solid which was filtered as before and dried in vacuo at room temperature for several hours. M.p. 238-240° with some prior decomposition. Anal. Calcd. for $ZrCl(C_6H_6O_2N)_3$: Cl, 7.10; Zr, 18.28. Found: Cl, 7.27; Zr, 17.90.

Synthesis of Pentahaptocyclopentadienyltris-(3-cyanoacetylacetonato)zirconium(IV)

Apparatus and techniques used were similar to those used before.

3-Cyanoacetylacetone (3.31g, 26.5 mmol) dissolved in 25 ml of benzene with triethylamine (1.87 ml, 13.4 mmol) was added dropwise to anhydrous dichlorobiscyclopentadienylzirconium(IV) (3.91g, 13.4 mmol) in 50 ml of benzene at 0°. At the completion of addition, the reaction mixture was stirred at room temperature for 47 hours. The white solid in the reaction mixture was filtered under anhydrous conditions, washed with 10 ml portions of benzene, and dried in vacuo at room temperature for several hours.

An nmr spectrum of this white product indicated mostly triethylammonium chloride with approximately 10% chelated β-diketone. The mixture was separated by heating in 35 ml of benzene for five minutes followed immediately by anhydrous filtration. The isolated solid was washed with 10 ml of benzene and dried in vacuo at room temperature for several hours. An nmr spectrum indicated pure triethylammonium chloride.

The filtrate from the mixture separation contained a few white crystals. Addition of 45 ml of hexane precipitated considerably

more white product. This mixture was stored at 5° for ten days. After warming to room temperature, the white, crystalline product was filtered under anhydrous conditions and dried in vacuo at room temperature for several hours. M.p. 200-204° with some prior decomposition. Anal. Calcd. for $Zr(h^5C_5H_5)(C_6H_6O_2N)_3$: C, 52.25; H, 4.39; Zr, 17.25. Found: C, 52.52; H, 4.51; Zr, 16.71.

Synthesis of Dichlorobis-(cyanobenzoylacetonato)-zirconium(IV)

Apparatus and techniques used were similar to those used before.

Cyanobenzoylacetone (2.31g, 12.4 mmol), dissolved in 25 ml of dichloromethane, was added dropwise to anhydrous zirconium tetrachloride (2.34g, 10.0 mmol) in 50 ml of dichloromethane at 0°. At the completion of addition, the reaction mixture was refluxed for 1.5 hours. The solid remaining after reflux was filtered under anhydrous conditions. The clear, pink filtrate was reduced in volume with mild heating under reduced pressure to approximately 25 ml. There were 60 ml of hexane added, the resulting white precipitate was anhydrously filtered, washed with two 10 ml portions of hexane, and dried in vacuo at room temperature for several hours. M.p. 192-194° with some prior decomposition. Anal. Calcd. for $ZrCl_2(C_{11}H_8O_2N)_2$: C, 49.44; H, 3.02; Cl, 13.27; Zr, 17.07. Found: C, 49.55; H, 3.33; Cl, 13.06; Zr, 17.27.

Synthesis of Tetrakis(3-cyanoacetylacetonato)-zirconium(IV)

Apparatus and techniques used were similar to those used before.

1. Chlorotris(3-cyanoacetylacetonato)zirconium(IV) (1g, 2 mmol) was added to 50 ml of water and stirred for two hours. The product was filtered in the open air, washed with water, and dried in vacuo at 80° for several hours. M.p. 273-276°; lit: 258.5°.[35] Anal. Calcd. for $Zr(C_6H_6O_2N)_4$: C, 49.05; H, 4.12; Cl, 0.00; Zr, 15.52. Found: C, 49.16; H, 4.19; Cl, 0.16; Zr, 15.78.

2. 3-Cyanoacetylacetone (3.55g, 28.4 mmol), dissolved in 25 ml of dichloromethane, was added dropwise to anhydrous zirconium tetrachloride (1.54g, 6.61 mmol) in 50 ml of dichloromethane at 0°. At the completion of addition, the reaction mixture was refluxed for four hours. The solid remaining after reflux was filtered under anhydrous conditions and washed with two 10 ml portions of dichloromethane. The clear filtrate was reduced in volume with mild heating under reduced pressure to about 25 ml. There were 50 ml of hexane added, the resulting white precipitate was anhydrously filtered, washed with two 10 ml portions of hexane, and dried in vacuo at room temperature for several hours. M.p. 273.5-275°. Anal. Calcd. for $Zr(C_6H_6O_2N)_4$: Zr, 15.52. Found: Zr, 15.46.

Attempted Preparation of Trichloro(3-cyanoacetylacetonato)-zirconium(IV)

Apparatus and techniques used were similar to those used before. Several unsuccessful attempts were made to form this product:

1. 3-Cyanoacetylacetone (3.00g, 24.0 mmol), dissolved in 25 ml of benzene, was added dropwise to anhydrous zirconium tetrachloride (5.54g, 23.8 mmol) in 50 ml of benzene at 0°. At the completion of addition, the reaction mixture was refluxed for one hour. The solid remaining after reflux was filtered under anhydrous conditions and dried *in vacuo* for several hours at room temperature. The clear and colorless filtrate contained no evidence of solids when reduced to dryness. M.p. decomposes at 240°. *Anal.* Calcd. for $ZrCl_3(C_6H_6O_2N)$: C, 22.40; H, 1.88; N, 4.35; Cl, 33.06; Zr, 28.36. Found: Cl, 25.69; Zr, 24.08.

2. 3-Cyanoacetylacetone (2.39g, 19.1 mmol), dissolved in 25 ml of benzene, was added dropwise to anhydrous zirconium tetrachloride (4.41g, 18.9 mmol) in 50 ml of benzene at 0°. At the completion of addition, the reaction mixture was stirred at 40° for 1.5 hours. The solid remaining after stirring was filtered under anhydrous conditions, washed with three 15 ml portions of benzene, and dried *in vacuo* for several hours at room temperature. The clear and colorless filtrate contained no evidence of solids when reduced to dryness. M.p. decomposes but does not melt below 300°. *Anal.* Found: Cl, 22.31; Zr, 22.22.

3. 3-Cyanoacetylacetone (2.46g, 19.7 mmol), dissolved in 25 ml of benzene, was added dropwise to anhydrous zirconium tetrachloride (4.58g, 19.7 mmol) in 50 ml of benzene at 0°. At the completion of addition, the reaction mixture was stirred at 40° for 1.5 hours. The solid remaining after stirring was filtered under anhydrous conditions, washed with two 15 ml portions of benzene, and dried *in vacuo* for several hours at room temperature. The clear and colorless filtrate contained no evidence of solids when reduced to dryness. M.p. 212-215° with some prior decomposition. *Anal.* Found: C, 30.39; H, 3.73; N, 4.09; Cl, 22.18; Zr, 21.92.

4. 3-Cyanoacetylacetone (1.23g, 9.84 mmol) was added to anhydrous zirconium tetrachloride (2.21g, 9.48 mmol) in 85 ml of hexane at 0°. The reaction mixture was refluxed for three hours. The solid remaining after reflux was filtered under anhydrous conditions and dried *in vacuo* for several hours at room temperature. The clear and colorless filtrate contained no evidence of solids when reduced to dryness. M.p. decomposes but does not melt below 300°. *Anal.* Found: Cl, 27.75; Zr, 28.92.

Alternate Methods Used in Attempting to Prepare Chlorotris-(3-cyanoacetylacetonato)zirconium(IV)

Apparatus and techniques used were similar to those used before. Two attempts were made to form this product:

1. 3-Cyanoacetylacetone (2.91g, 23.3 mmol), dissolved in 25 ml of dichloromethane, was added dropwise to anhydrous zirconium tetrachloride (1.77g, 7.60 mmol) in 50 ml of dichloromethane at 0°. At the completion of addition, the reaction mixture was stirred for 18 hours, then refluxed for 2 hours. The solids remaining after reflux were filtered under anhydrous conditions. The clear filtrate

was reduced in volume; 50 ml of hexane were added whereupon a large amount of white solid precipitated. The volume was further reduced to 50 ml and the solid product was filtered under anhydrous conditions and dried *in vacuo* for several hours. M.p. 246° with significant prior decomposition. *Anal.* Calcd. for $ZrCl(C_6H_6O_2N)_3$: Cl, 7.10; Zr, 18.28. Found: Cl, 4.93; Zr, 17.40.

2. Tetrakis(3-cyanoacetylacetonato)zirconium(IV) (0.88g, 1.49 mmol), dissolved in 25 ml of dichloromethane, was added dropwise to dichlorobis(3-cyanoacetylacetonato)zirconium(IV) (0.61g, 1.49 mmol) in 50 ml of dichloromethane at 0°. At the completion of addition, the reaction mixture was stirred for 42 hours; one ml of hexane was added, and resulting solids were removed by filtration under anhydrous conditions. Enough hexane was added to the cloudy filtrate to bring the solvent mixture to 1:1 dichloromethane: hexane. The resulting white product was filtered under anhydrous conditions, washed with 15 ml of hexane, and dried *in vacuo* for several hours. M.p. 240-243° with some prior decomposition. An infrared spectrum indicates two bands in the C-N region: 2220 cm^{-1} (very strong) and 2250 cm^{-1} (medium).

Characterization of Compounds

Melting Points

Melting points were measured in sealed capillaries using a Hoover-Thomas melting point apparatus.

Chloride Analysis

Approximately 0.25g of sample was weighed into a 25 ml Erlenmeyer flask tared with a rubber septum and a magnetic stirring

bar. The sample flask was sealed with the septum prior to exit from the Dri-Lab.[34] After determining the sample weight, a syringe was used to inject 10 ml of distilled water through the septum while a second syringe was used to withdraw an equivalent volume of air. Both syringes were removed; the syringe containing the extracted vapor was sealed with a cork on the tip. The contents of the flask were stirred for several minutes; the flask was opened while five pellets of NaOH were rapidly added and resealed; and stirring was continued until the complex decomposed.

The solution was washed into a 200 ml tall-form beaker, and diluted to 100 ml with distilled water. While stirring the solution, the gas in the syringe was slowly injected into the solution. There were two drops of bromcresol green indicator added, and the solution was acidified with 6N HNO_3 until the color changed from blue to yellow. An excess of six drops of acid were added. A potentiometric titration was carried out using a glass electrode as the reference electrode, a silver electrode as the indicator electrode, and a pH meter. Silver nitrate (0.1N) was added with a 50 ml buret, and the potential was followed as a function of the volume of titrant added. A plot of the potential versus milliliters of titrant delivered yields the end-point which was used to calculate the percent chloride.

Zirconium Analysis

The amount of zirconium present was determined as ZrO_2 from the hydrolysis and subsequent ignition of the compound. About 0.2g of the compound to be analyzed was placed in a platinum crucible which had been brought to constant weight. To the sample was added approximately 10 ml of 15% NH_4OH solution. The crucible

was placed in an oven at 90-95° overnight or until only dry, solid hydrolysis products remained. The crucible was then heated cautiously with a bunsen burner until fumes were no longer released. Finally, the sample and crucible were repeatedly ignited at 1000° for 30 minutes and cooled in a dessicator for 30 minutes until a constant weight had been reached. The mass of zirconium was determined as 74.03% of the white ZrO_2.

Carbon, Hydrogen and Nitrogen Analysis

Analyses of air sensitive compounds were done by Schwarzkopf Microanalytical Laboratory, Woodside, New York. All others were done by Atlantic Microlab, Inc., Atlanta, Georgia.

Infrared Absorption Spectra

Infrared spectra were recorded in the 4000-250 cm^{-1} region with a Perkin-Elmer Model 457 double beam-grating spectrophotometer. The instrument was calibrated with atmospheric CO_2 at 2367 and 2336 cm^{-1}. All products are solid and as such were examined as Nujol mulls supported between potassium bromide plates. The maximum uncertainty in the reported frequencies is estimated to be less than 5 cm^{-1}.

Nuclear Magnetic Resonance Spectra

Proton chemical shifts were obtained with a Hitachi Perkin-Elmer R-20B spectrometer at 60 MHz at 35°. Samples were dissolved in $CDCl_3$ except where noted.

CHAPTER III

DISCUSSION AND RESULTS

Preparative Chemistry

Zirconium tetrachloride ($ZrCl_4$) and dichlorobispentahapto-cyclopentadienylzirconium(IV) ($(C_5H_5)_2ZrCl_2$) react with 3-cyanoacetylacetone in inert anhydrous organic solvents to give enolate derivatives plus hydrogen chloride. In refluxing dichloromethane, the 3-cyanoacetylacetonate complexes dichlorobis(3-cyanoacetylacetonato)-zirconium(IV), ($ZrCl_2(CAA)_2$), chlorotris(3-cyanoacetylacetonato)-zirconium(IV), ($ZrCl(CAA)_3$), and tetrakis(3-cyanoacetylacetonato)-zirconium(IV), ($Zr(CAA)_4$), can be isolated. At room temperature in benzene containing triethylamine, the reaction of $(C_5H_5)_2ZrCl_2$ and 3-cyanoacetylacetone yields $Zr(C_5H_5)(CAA)_3$ plus triethylammonium chloride and cyclopentadiene. Also, in a manner similar to that of $ZrCl_2(CAA)_2$, dichlorobis(cyanobenzoylacetonato)zirconium(IV), ($ZrCl_2(CNbzac)_2$), was prepared. Dichlorobis(cyanodibenzoylmethanato)-zirconium(IV) was unable to be prepared.

When a 1:2 ratio of $ZrCl_4$ and 3-cyanoacetylacetone was used in attempts to prepare dichlorobis(β-diketonato)zirconium(IV), the low chloride analysis of the isolated product indicated the probable

predominant formation of the chlorotris(β-diketonato)zirconium(IV). Therefore, only a 1:1 ratio of $ZrCl_4$ and 3-cyanoacetylacetone was used in order to minimize the possible formation of the chlorotris-(β-diketonato)zirconium(IV). After refluxing in dichloromethane, the unreacted and/or undissolved solids were filtered, and the dichlorobis(β-diketonato)zirconium(IV) product was precipitated by the addition of hexane after the volume of the dichloromethane solution had been significantly reduced.

In the synthesis of $ZrCl(CAA)_3$, it was nearly impossible to prevent the concurrent formation of the tetrasubstituted product, $Zr(CAA)_4$. Reaction of $ZrCl_4$ and 3-cyanoacetylacetone in a 1:1.8 ratio in dichloromethane also left unreacted and/or undissolved solids. The filtrate from the isolation of those solids precipitated more solids on standing overnight at 5°. The filtrate obtained from isolation of the precipitate was reduced to dryness and the solids were resuspended with a 1:1 dichloromethane: hexane mixture. The isolation of these resuspended solids gave a filtrate which when reduced in volume precipitated the desired product, $ZrCl(CAA)_3$, upon addition of hexane.

Several attempts to obtain $ZrCl(CAA)_3$, including some ten different combinations of dichloromethane and hexane in the precipitation of solids from the filtrates, were not wholly successful. Chloride and infrared spectral analyses implied that in many cases these solids were mixtures of the tris- and tetrasubstituted products, $ZrCl(CAA)_3$ and $Zr(CAA)_4$.

The inability to repeat the successful preparation of $ZrCl(CAA)_3$ seems to be due to the difficulty in isolating $ZrCl(CAA)_3$ from such a mixture. This may be the result of the decomposition in solution of the type[36]:

$$4ZrCl(CAA)_3Cl \rightleftharpoons 3Zr(CAA)_4 + ZrCl_4 \quad \text{and}$$

$$2ZrCl(CAA)_3 \rightleftharpoons ZrCl_2(CAA)_2 + Zr(CAA)_4 .$$

This is consistent with the observations made on the infrared spectrum of the product isolated from the reaction of $ZrCl_2(CAA)_2$ and $Zr(CAA)_4$ in a 1:1 ratio: a large peak at 2220 cm^{-1} with a significantly less intense peak at 2250 cm^{-1} may indicate some $ZrCl(CAA)_3$ but apparently the tetrasubstituted $Zr(CAA)_4$ is predominant. Furthermore, the product obtained from the reaction of $ZrCl_4$ and 3-cyanoacetylacetone in a 1:3 ratio, while exhibiting C-N stretching bands in the infrared spectrum quite similar to those observed for $ZrCl(CAA)_3$, has a chloride content of only 4.93% and a zirconium content of 17.40%. This also implies a mixture of $ZrCl(CAA)_3$ and $Zr(CAA)_4$.

Efforts to prepare chloropentahaptocyclopentadienylbis(3-cyanoacetylacetonato)zirconium(IV), $[ZrCl(C_5H_5)(CAA)_2]$, were also unsuccessful. It has been reported that the reaction of $(C_5H_5)_2ZrCl_2$, β-diketone, and triethylamine in a 1:2:1 mole ratio in acetonitrile results in the formation of $ZrCl(C_5H_5)(diketonato)_2$.[37]

However, an attempt to prepare $ZrCl(C_5H_5)(CAA)_2$ in this manner yielded only the trisubstituted product $Zr(C_5H_5)(CAA)_3$ and mixtures of this with $Zr(CAA)_4$. Also found were large amounts of $ZrCl_2(C_5H_5)_2$ starting material.

The tetrasubstituted product, $Zr(CAA)_4$, was prepared by two methods:

1. by stirring $ZrCl(CAA)_3$ in water for several hours, filtering the product, and drying it for several hours in vacuo at 80°, and

2. by reacting $ZrCl_4$ and 3-cyanoacetylacetone in a 1:4 ratio in refluxing dichloromethane, filtering off the unreacted and/or undissolved solids, reducing the volume of the filtrate, and precipitating the product by the addition of hexane.

The ease with which the tetrasubstituted product was observed to form contrasts significantly with its acetylacetonate analog. It has been reported that $Zr(acac)_4$ cannot be prepared by reaction of $ZrCl_4$ with excess acetylacetone under anhydrous conditions; even after prolonged heating, the highest substitution product obtained was $ZrCl(acac)_3$.[38] Others have found that heating $ZrCl(acac)_3$ with neat acetylacetone (1:40 molar ratio) for 24 hours at 80° yields a product which is ca. 20% $Zr(acac)_4$.[28] Thus, the fourth chlorine atom can be replaced by acetylacetone under anhydrous conditions, but the rate of substitution is slow. The ready conversion of

$ZrCl(acac)_3$ to $Zr(acac)_4$ by stirring in water has been reported, however.[38]

In anhydrous media, the ease of complete substitution is apparently strongly dependent on the nature of the diketone, since certain fluoroacetylacetones[39] and 3-cyanoacetylacetone readily afford the tetrakisdiketonates. Apparently, these more acidic diketones are more effective in replacing the last zirconium-bonded chloride.[31]

Attention is directed to a serious discrepancy between the melting point reported in this work and that of an earlier literature preparation for $Zr(CAA)_4$. (See Experimental Section.) Foll[35] prepared tetrakis(3-cyanoacetylacetonato)zirconium(IV) by dissolving 25 parts 3-cyanoacetylacetone in 250 parts of water containing nine parts NaOH, and the solution was neutralized with acetic acid. The filtered solution was added to a filtered solution of 16.1 parts $ZrOCL_2$ in water. The precipitated chelate was dried in air over calcium chloride and recrystallized from boiling toluene. The observed melting point of this product was reported as 258.5°. The agreement between the melting points for $Zr(CAA)_4$ prepared in this work in both aqueous and anhydrous media, the elemental analytical results, and the spectra of these products (see later discussion) lead one to favor the higher melting point at 273 to 275°.

On the basis of the tin and titanium analogs reported earlier,[4] attempts were made to prepare trichloro(3-cyanoacetylacetonato)zirconium(IV). It was thought that the product would have

properties similar to those found for the tin and titanium analogs, i.e., a cyclic tetramer consisting of four octahedra, each having a sixth site filled by a nitrile group of a planar, trifunctional, bridging 3-cyanoacetylacetonate ligand oxygen chelated to an adjacent zirconium center (Figure 7). However, reaction of a 1:1 mole ratio of zirconium tetrachloride: 3-cyanoacetylacetone in dichloromethane (the method used in preparing the tin and titanium compounds) led to the isolation of the disubstituted product. There were three different attempts made with the same reagent combination in benzene which gave products having elemental analyses not corresponding to any reasonable empirical formulas. The Cl:Zr ratio in these products ranged from 2.58 to 2.81; of course the ratio for the monosubstituted product should be 3.00. It was thought that perhaps the $ZrCl_3$(CAA) complex was trapping a molecule of benzene upon formation of the product. Calcd. for $ZrCl_3$(CAA): Cl, 33.06; Zr, 28.36; for $ZrCl_3$(CAA).C_6H_6: Cl, 26.60; Zr, 22.81.) In one instance, a zirconium analysis of one of these products indicated a zirconium content of 22.22%; in another product, a chloride content of 25.69% was found. In the latter case, additional drying of the product in vacuo at 100° raised the chloride content to 28.96%; this might be consistent with benzene contamination.

An attempt to prepare $ZrCl_3$(CAA) in hexane gave a product with a higher cloride and zirconium content, but the Cl:Zr ratio was only 2.47.

Characterization of the
Cyano-β-Diketonate Complexes

The infrared spectra of $ZrCl_2(CAA)_2$, $ZrCl_2(CNbzac)_2$, $ZrCl(CAA)_3$, $Zr(C_5H_5)(CAA)_3$, and $Zr(CAA)_4$ are presented in Figures 13 through 17, respectively. In the chelating carbonyl region (1500 to 1600 cm^{-1}), they are generally similar to spectra of other zirconium acetylacetonates where the C===O and C===C modes absorb strongly.[11] No bands were observed in the 1600 to 1750 cm^{-1} region where the enol form of 3-cyanoacetylacetone absorbs strongly.[9] Therefore, both carbonyl groups are coordinated. Chelation by all 3-cyanoacetylacetonate ligands initially might lead one to think that the $ZrCl_2(CAA)_2$, $ZrCl(CAA)_3$, $Zr(C_5H_5)(CAA)_3$, and $Zr(CAA)_4$ complexes are respectively, six-, seven-, seven-, and eight-coordinate in the solid state. Indeed, molecular weight and conductance experiments of the similar zirconium acetylacetonate complexes[28] show that these complexes do have these coordination numbers.

However, the C-N stretching frequencies of these compounds, listed in Table 6, alter this conclusion. It has been shown that coordination of nitriles to metal centers through nitrogen gives a characteristic increase in $\nu_{C\equiv N}$ relative to the free nitrile. The bands observed at 2255 cm^{-1} and 2253 cm^{-1} for $ZrCl_2(CAA)_2$ and $ZrCl(CAA)_3$, respectively, are interpreted as being due to interaction of the cyanide group of a planar, oxygen chelated 3-cyanoacetylacetone ligand with the metal center of a second monomeric unit. This

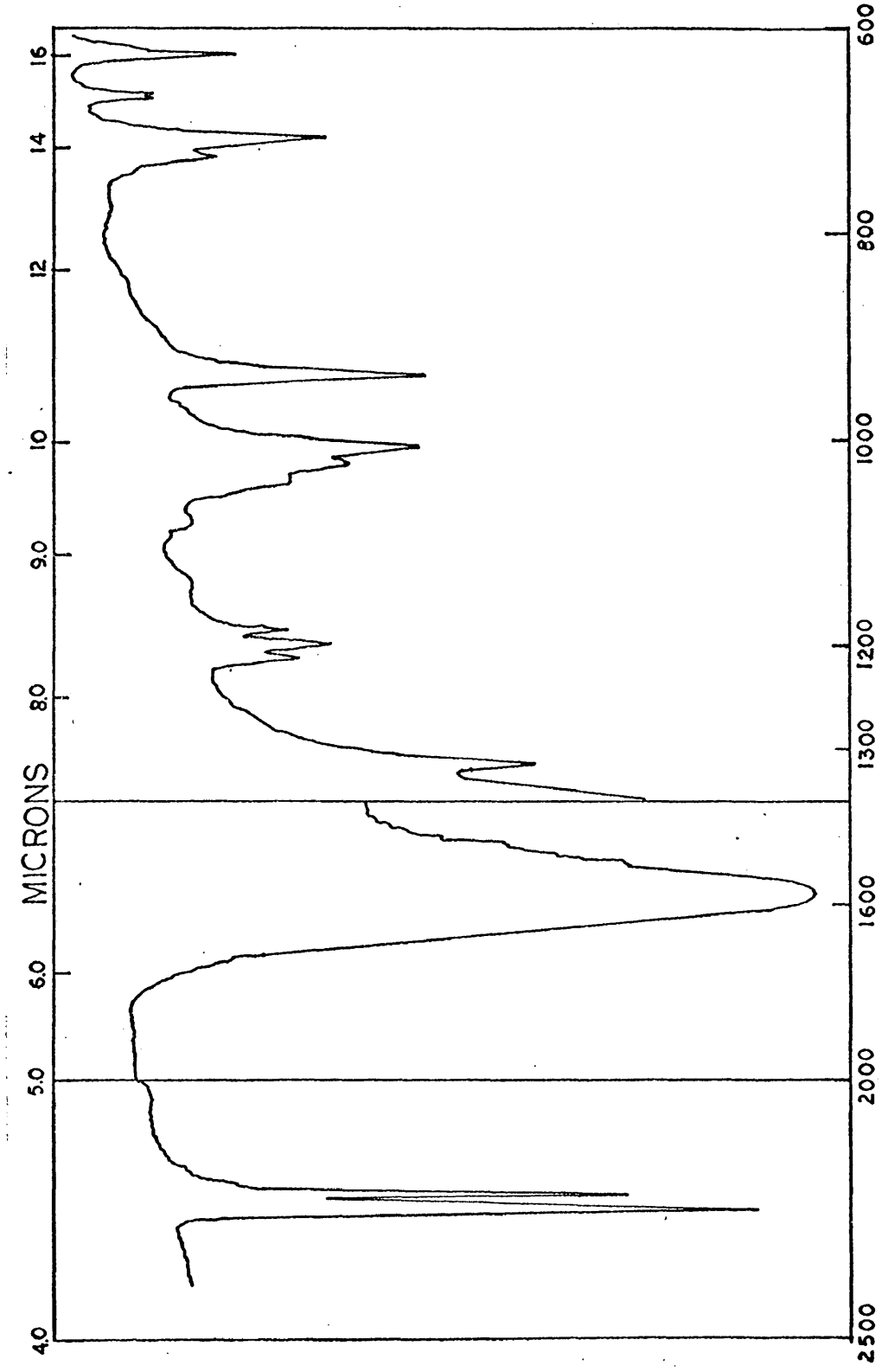


Figure 13

Infrared spectrum of dichlorobis(3-cyanoacetylacetonato)zirconium(IV) as a mull in Nujol

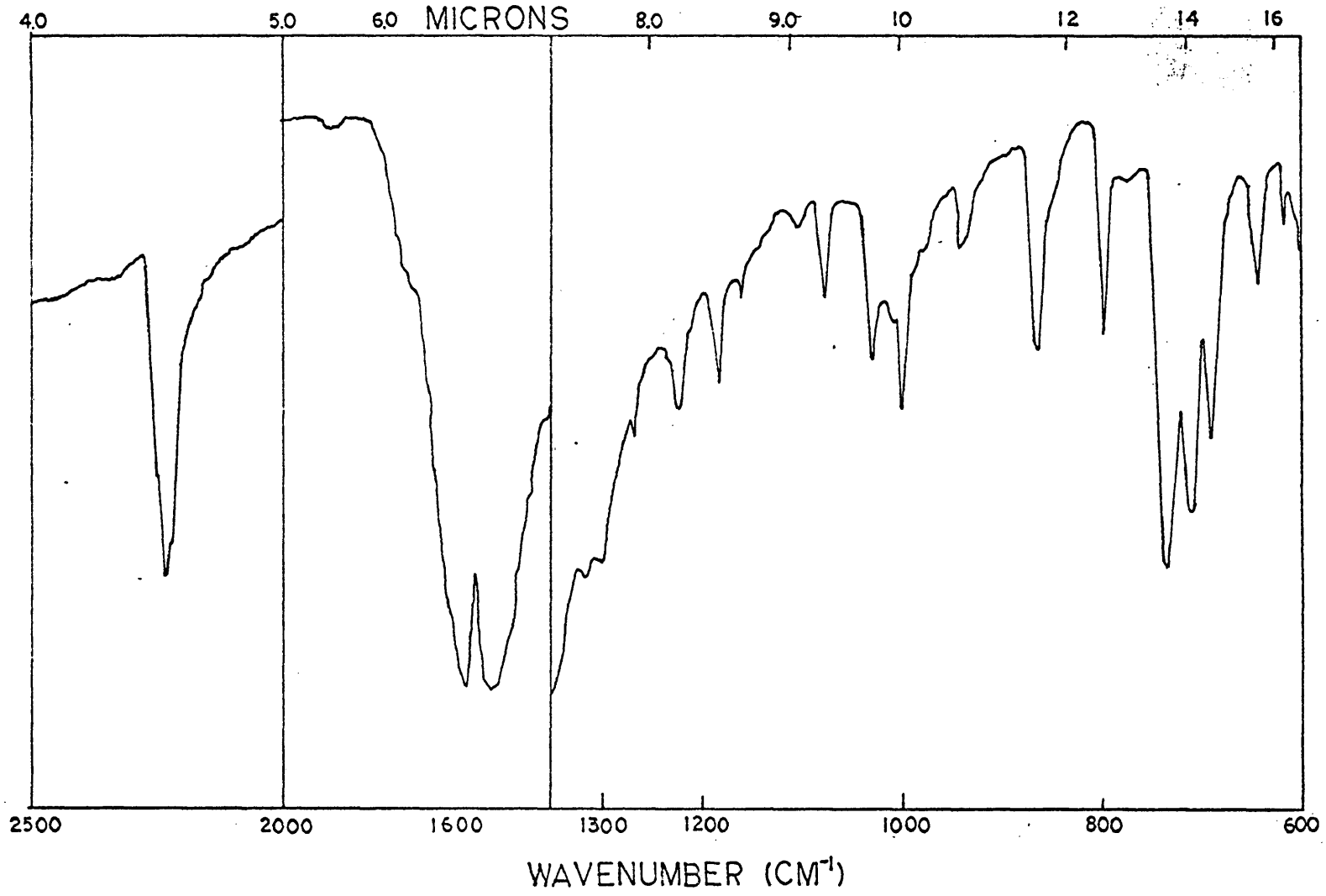


Figure 14

Infrared spectrum of dichlorobis(cyanobenzoylacetonato)zirconium(IV) as a mull in Nujol

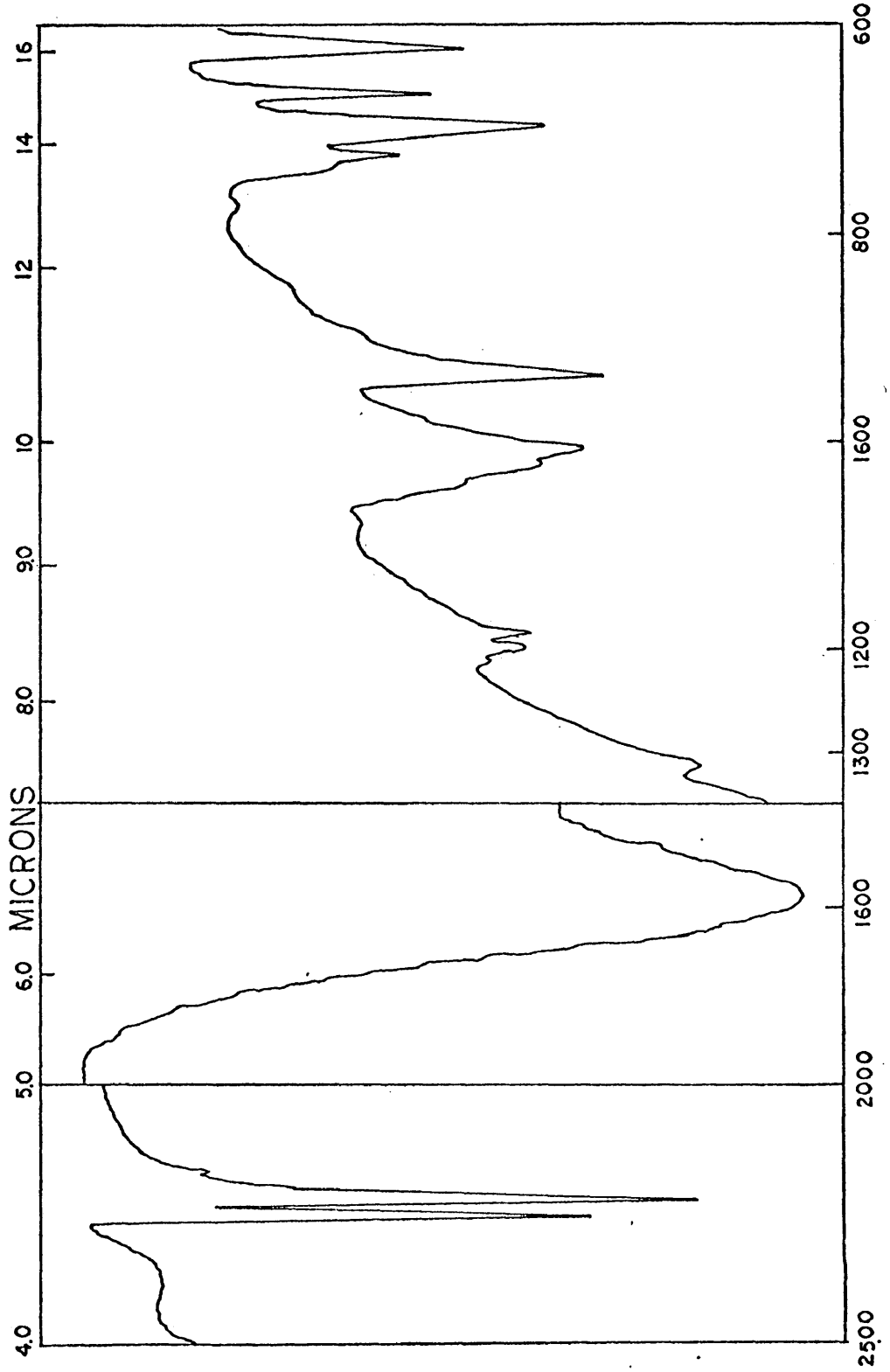


Figure 15

Infrared spectrum of chlorotris(3-cyanoacetylacetonato)zirconium(IV) as a mull in Nujol

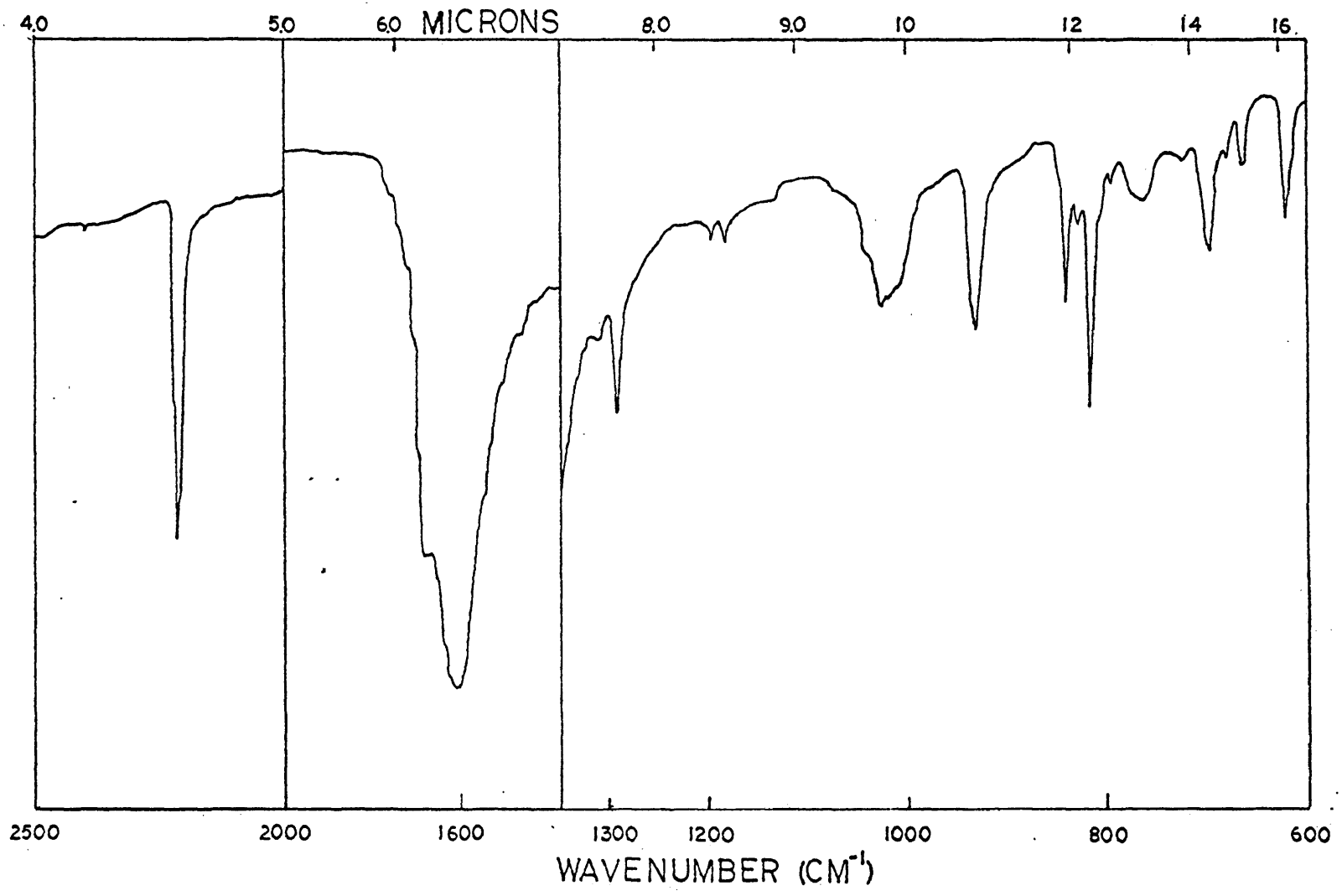


Figure 16

Infrared spectrum of pentahaptocyclopentadienyltris(3-cyanoacetylacetonato)-zirconium(IV) as a mull in Nujol

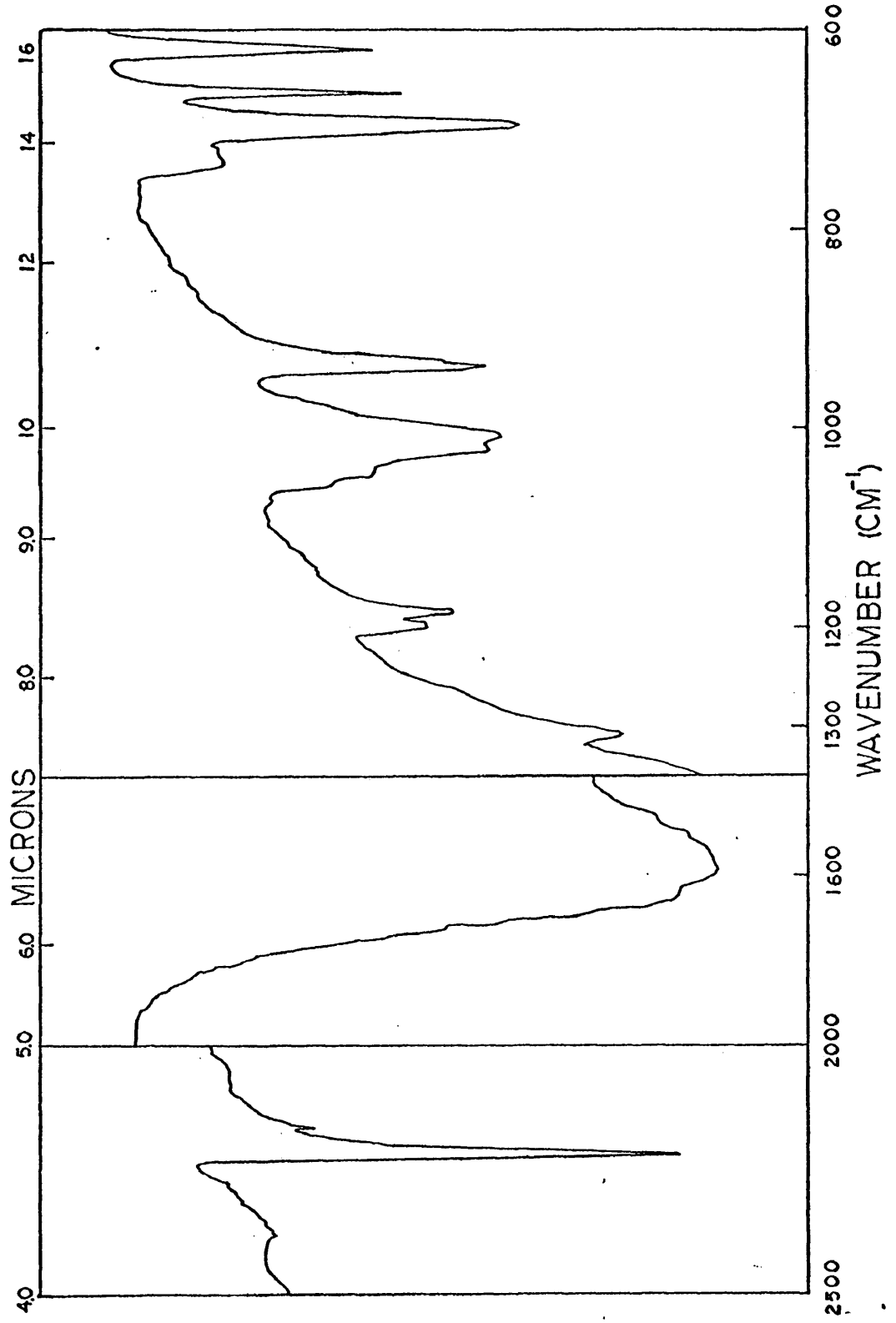


Figure 17

Infrared spectrum of tetrakis(3-cyanoacetylacetonato)zirconium(IV) as a mull in Nujol

TABLE 6

C-N stretching frequencies observed in cyano-β-diketonate complexes of zirconium(IV)[a]

Compound	C-N stretching frequencies (cm^{-1})[b]
3-cyanoacetylacetone	2219
cyanobenzoylacetone	2220
$ZrCl_2(CAA)_2$	2255, 2222
$ZrCl_2(CNbzac)_2$	2240 (2261, 2219)[c]
$ZrCl(CAA)_3$	2253, 2221
$Zr(C_5H_5)(CAA)_3$	2222 (2225, 2219)[c]
$Zr(CAA)_4$	2219

[a]Samples suspended between KBr plates as a Nujol mull

[b]Frequencies reported ±5 cm^{-1}

[c]Shoulders of main band

coordination of the nitrogen to the zirconium apparently increases the coordination number of the monomeric unit by one to seven and eight, respectively. The unshifted bands observed in these two complexes indicate the existence of non-bridging ligands as well. $Zr(CAA)_4$, which is coordinatively saturated, i.e., coordination number eight, exhibits a single unshifted cyanide peak as expected and supports this assumption.

The relative intensities of the shifted and unshifted bands yield further evidence as to the structure of these compounds. It has been shown that in alkyl and phenyl cyanide adducts of group (IV) metal chlorides both the frequency and intensity of the C-N stretching show characteristic increases.[22,40,41] From the infrared spectrum of $ZrCl_2(CAA)_2$, in which two bands are observed, one can infer that the shifted, more intense peak indicates one bridging ligand and that the unshifted, less intense peak indicates a non-bridging ligand. The spectrum of $ZrCl(CAA)_3$ also contains two C-N stretching bands. However, in this case, the shifted peak is less intense than the unshifted peak. Accordingly, it is concluded that of the three ligands, only one is involved in bridging to an adjacent metal center; the other two are apparently non-bridging.

The information contained in the infrared spectra of these complexes may be used to postulate structures. It has been shown that in the disubstituted product $ZrCl_2(CAA)_2$, the zirconium is probably seven-coordinate, with the seventh site containing a bridging

cyanide group from a ligand which is oxygen chelated to an adjacent zirconium. Furthermore, of the two ligands, one is engaged in this same type of bridging to another zirconium, while the second remains free. Since seven-coordinate zirconium acetylacetonates often possess the basic pentagonal bipyramidal stereochemistry,[31] the same basic geometry is suggested for $ZrCl_2(CAA)_2$. The precedent established earlier for cyclic oligomeric structures in bridged cyanides makes it reasonable to assume a cyclic oligomer here. As can be seen in Figure 18, a cyclic pentamer can be drawn which satisfies all of the conditions requisite to the analytical and spectral evidence discussed so far.

The disubstituted product, $ZrCl_2(CNbzac)_2$, might be expected to be structurally similar to its 3-cyanoacetylacetonate analog. However, its infrared spectrum is substantially different. Instead of two distinct bands in the C-N region, only one broad band centered at 2242 cm^{-1} with shoulders at 2219 cm^{-1} and 2261 cm^{-1} is observed. Although a shift appears to have occurred, it is not as great as that observed previously ($\Delta\nu_{C\equiv N}$ = 23 cm^{-1} as opposed to $\Delta\nu_{C\equiv N}$ = 36 cm^{-1}). Furthermore, the existence of the two shoulders and the absence of a distinct uncoordinated nitrile frequency complicates the problem even more. The shoulder at 2219 cm^{-1} may be a non-bridging nitrile; however, ambiguity exists. Therefore, the analytical results allows one to verify the empirical formula, $ZrCl_2(CNbzac)_2$, but the suggestion of a reasonable structure

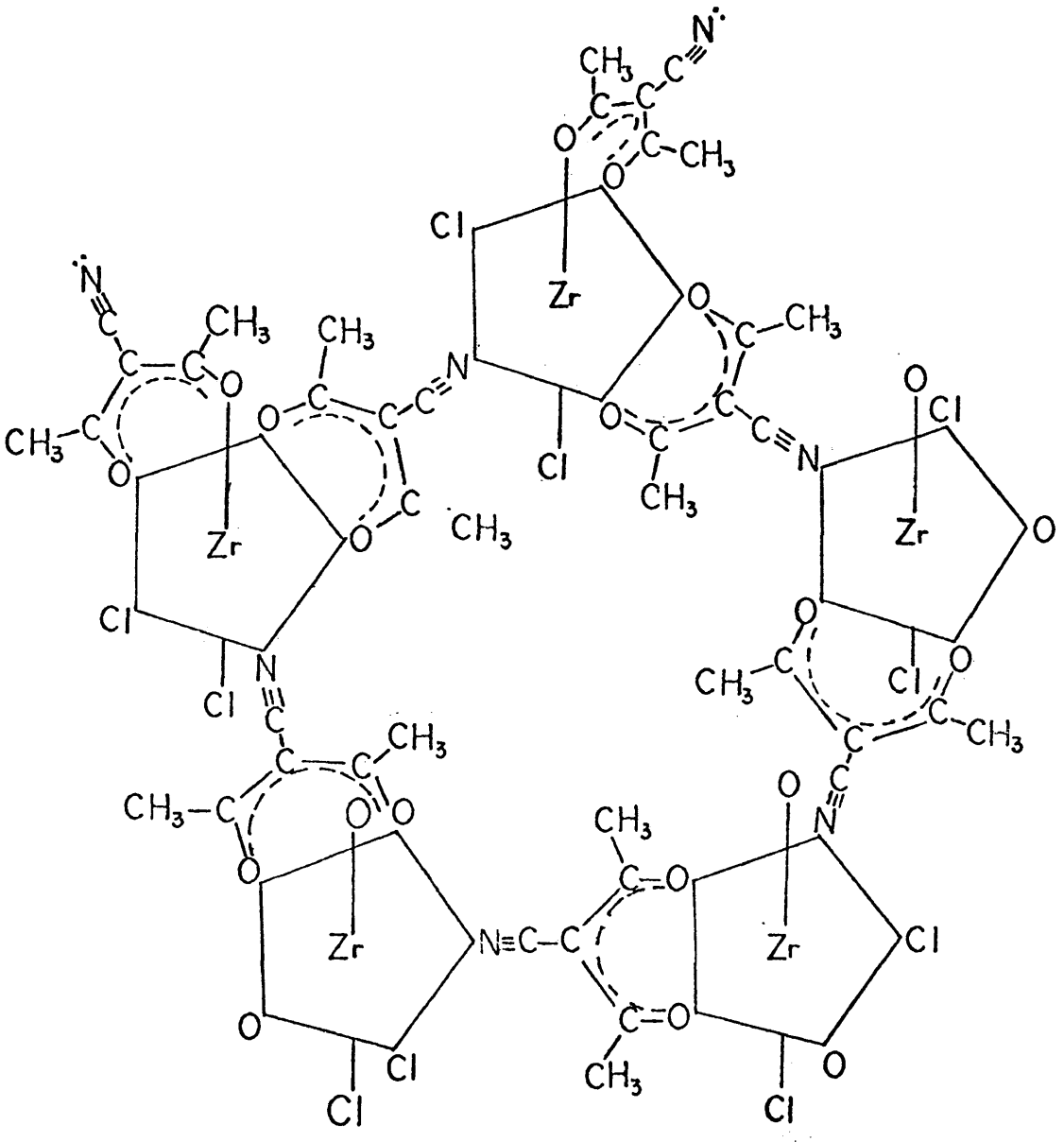


Figure 18

The postulated structure of
dichlorobis(3-cyanoacetylacetonato)zirconium(IV)
(Some chelate rings omitted for clarity)

according to the evidence obtained thus far seems premature.

In the trisubstituted product, $ZrCl(CAA)_3$, the complex is probably eight-coordinate, with one site available for bridging. Furthermore, of the three ligands, one is engaged in bridging to another zirconium, while the other two remain free. Since eight-coordinate $Zr(acac)_4$ exhibits the square antiprismatic structure,[42,43] the same geometry is assumed here. Again, assuming a cyclic, rather than an open chain oligomer, three reasonable structures are possible, depending on the location of the eighth bridging site within the monomeric unit. The possible monomeric units making up the postulated cyclic trimer tetramer, and pentamer are presented in Figures 19a, 19b, and 19c, respectively. The monomer shown in Figure 19d is the basic structure of a linear chain. The complexity of the oligomeric molecules prevents the presentation of clear figures. Molecular models have been used to postulate these structures.

The second trisubstituted product, $Zr(h^5C_5H_5)(CAA)_3$ has a band with two shoulders in the unshifted C-N region of the infrared spectrum. This is consistent with seven-coordination in which none of the three ligands are involved in trifunctional bridge bonding. As with pentahaptocyclopentadienylbis(acetylacetonato)-zirconium(IV),[31] $Zr(C_5H_5)(CAA)_3$ is thought to have a pentagonal bipyramidal geometry in which the center of the cyclopentadienyl ring occupies an axial vertex (see Figure 20). The basic nature of the infrared spectrum does not indicate interaction between a

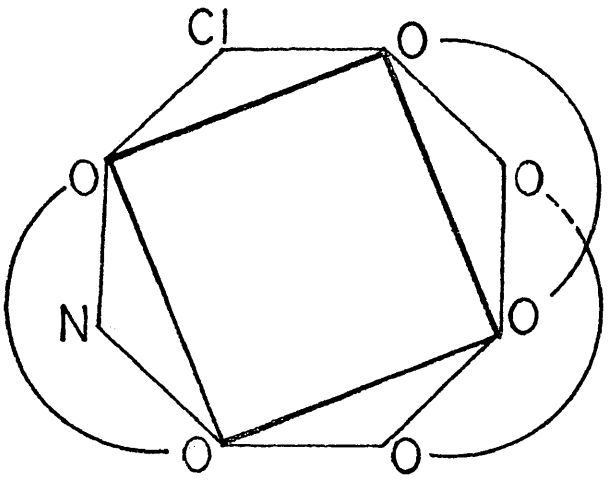


Figure 19a
Monomeric unit of possible cyclic trimer

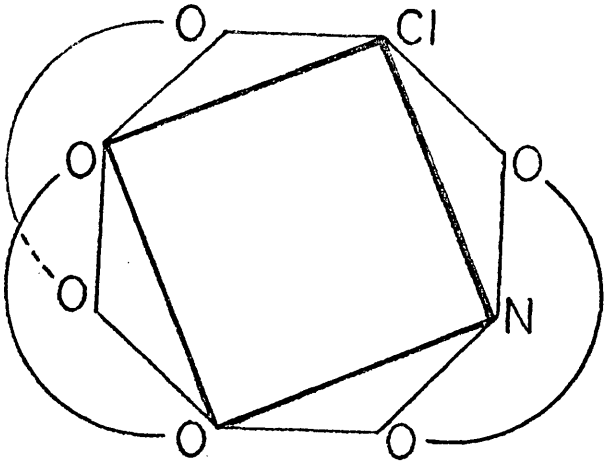


Figure 19b
Monomeric unit of possible cyclic tetramer

Figure 19

The structure of chlorotris(3-cyanoacetyl-acetonato)zirconium(IV). (Carbon skeleton of chelate rings omitted for clarity; vacant site available for cyanide bridging denoted by N)

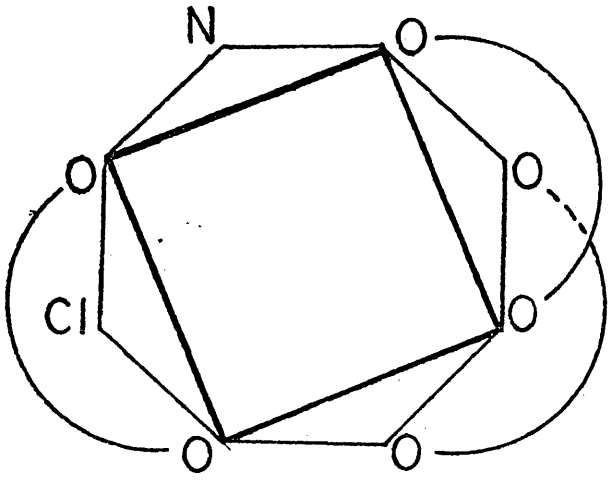


Figure 19c
Monomeric unit of possible cyclic pentamer

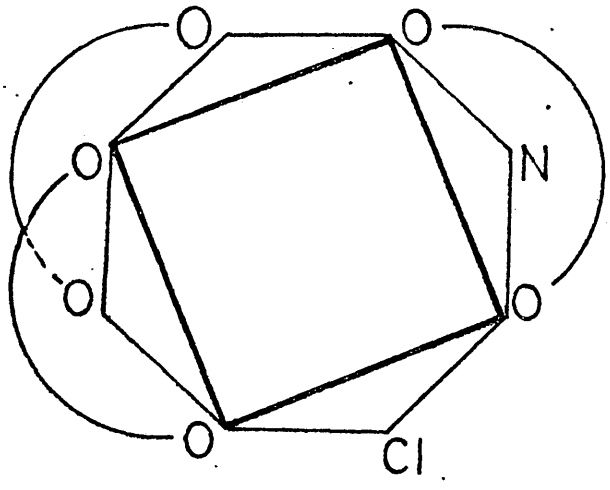


Figure 19d
Monomeric unit of possible linear chain

Figure 19 (continued)

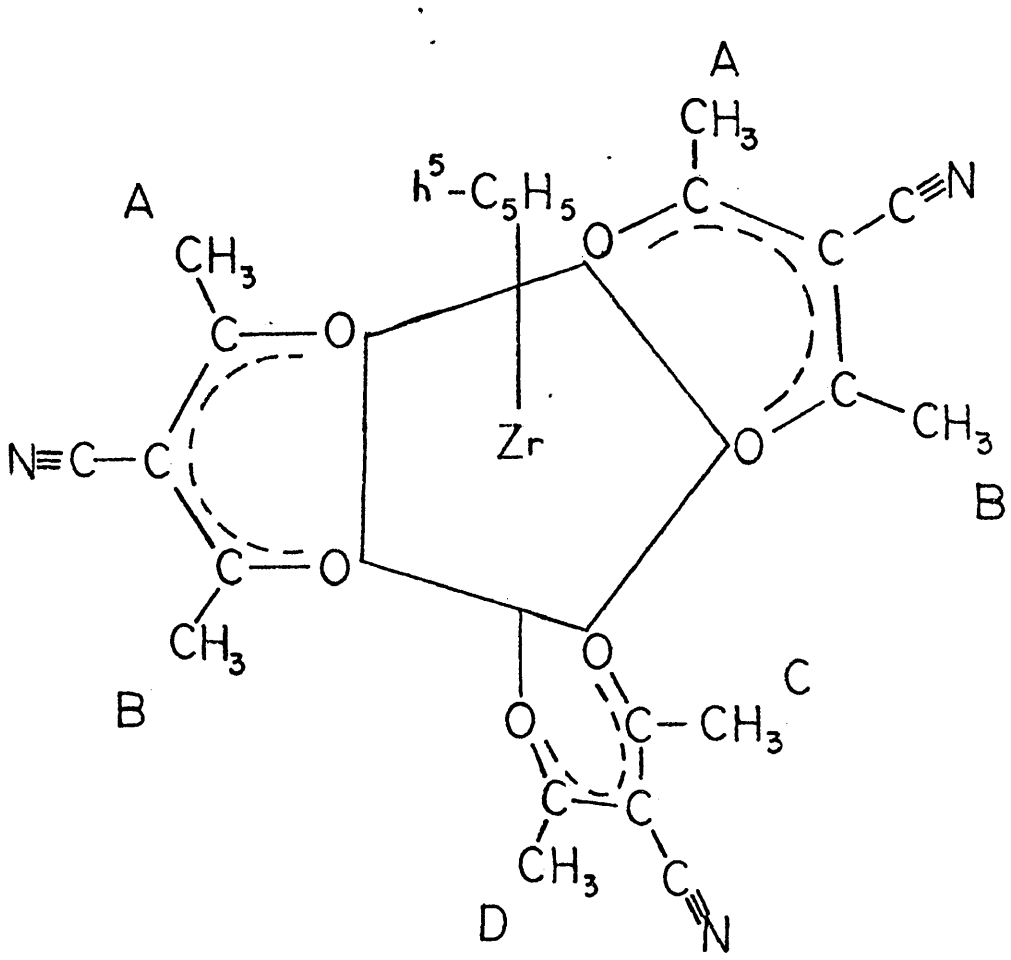


Figure 20

The stucture of pentahaptocyclopentadienyl-tris(3-cyanoacetylacetonato)zirconium(IV)

nitrile group and a zirconium center. This may be a result of the large steric requirements of the pi-bonded cyclopentadienyl ring preventing bridging of a cyanide from an adjacent unit to an eighth coordination site. The C_s symmetry of this structure is consistent with three modes of C-N stretching which are expected in the 2220 cm^{-1} region; two shoulders are observed on the cyanide band.

The tetrasubstituted product $Zr(CAA)_4$ is eight-coordinate. Since eight is in the maximum coordination number that a zirconium center can have, one expects no bridging nitrile groups. The infrared spectrum of this compound contains only a single C-N peak indicating that such a prediction is correct. A square antiprism in which all coordination sites are occupied by chelating oxygens is suggested (Figure 21).

The problems experienced in trying to characterize the product obtained in attempting to make $ZrCl_3(CAA)$ are further complicated by the infrared spectral data. The products isolated from benzene exhibit a single C-N stretching frequency at 2250 cm^{-1}, implying the presence of only coordinated nitriles. On the other hand, the product obtained from hexane exhibits a single sharp peak at 2226 cm^{-1} with only a slight shoulder at 2240 cm^{-1}. This seems to indicate predominantly uncoordinated nitriles. Obviously, the poor analytical results and the conflicting spectral evidence preclude any conclusions regarding the nature of these products.

The methyl regions of the nuclear magnetic resonance spectra

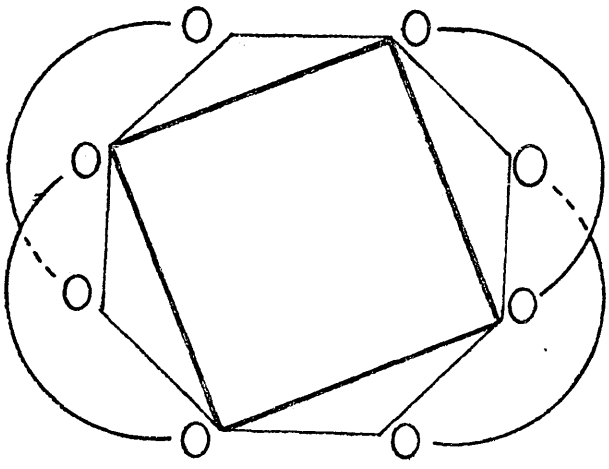


Figure 21

The structure of tetrakis(3-cyanoacetylacetonato)zirconium(IV). (Carbon skeleton of chelate rings omitted for clarity.)

of 3-cyanoacetylacetone, $ZrCl_2(CAA)_2$, $ZrCl(CAA)_3$, $Zr(C_5H_5)(CAA)_3$, and $Zr(CAA)_4$ are presented in Figures 22 through 26. Table 7 lists the peaks observed in this work and for comparison, those reported for the acetylacetonate analogs. Attention is directed to the trend of a decreasing value of $\delta(CH_3)$ as the number of chelating ligands is increased from two to four. This pattern, reported earlier for zirconium acetylacetonates,[28] seems to remain consistent with the zirconium 3-cyanoacetylacetonates as well.

Although the $ZrCl_2(acac)_2$ cis isomer contains two sets of methyl protons, the observation of a single methyl resonance indicates that the chelate rings undergo rapid configurational rearrangements which exchange methyl groups between the various nonequivalent environments. Even at -130° only one rather sharp methyl resonance was observed. Consequently, one might expect a single methyl proton resonance peak in the nmr spectrum of $ZrCl_2(CAA)_2$ at 35°.

However, two peaks are apparent. Observations made during attempts to prepare $ZrCl(CAA)_3$ indicate that in solution there exists an equilibrium between $ZrCl_2(CAA)_2$ and $ZrCl(CAA)_3$. Therefore, it is suggested that the larger upfield peak is due to the methyl proton resonance of $ZrCl(CAA)_3$ formed by the reaction:

$$3ZrCl_2(CAA)_2 \rightleftharpoons 2ZrCl(CAA)_3 + ZrCl_4 \ .$$

(Note the close correspondence of this chemical shift with that reported for $ZrCl(CAA)_3$.) Precedent for this type of decomposition

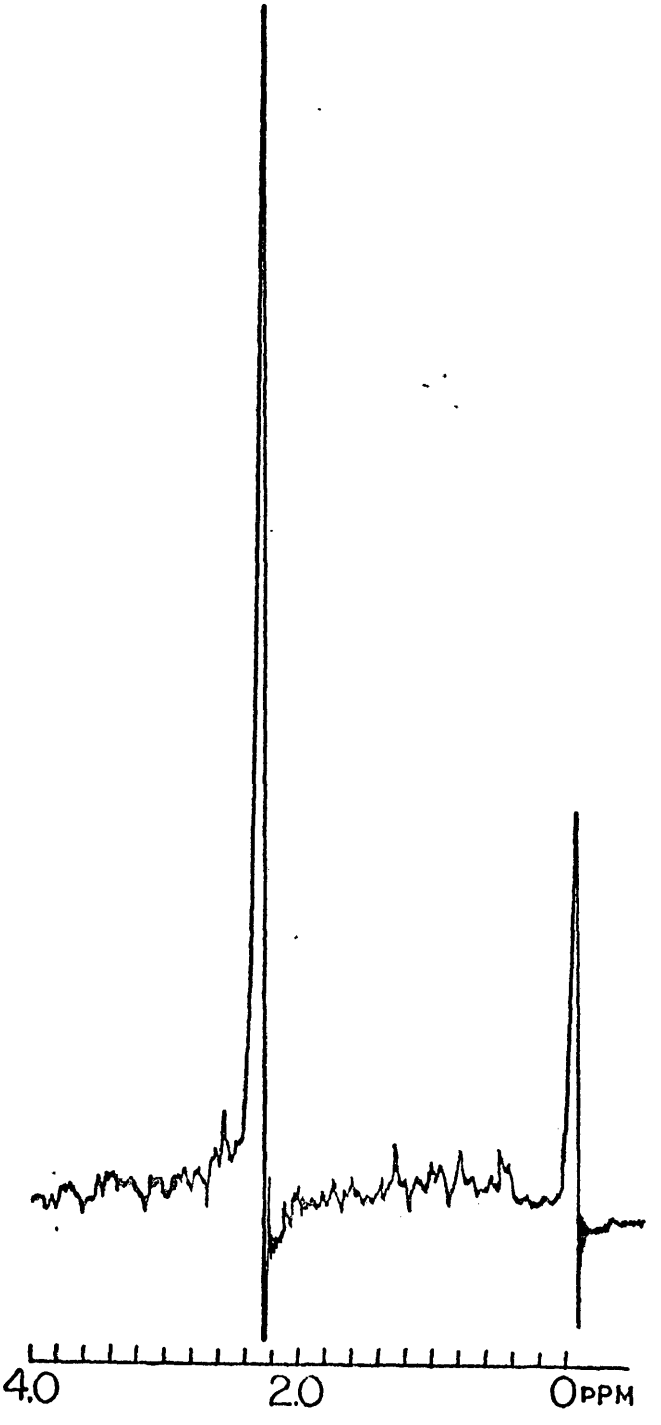


Figure 22

The methyl proton resonance observed in the nmr spectrum of 3-cyanoacetylacetone

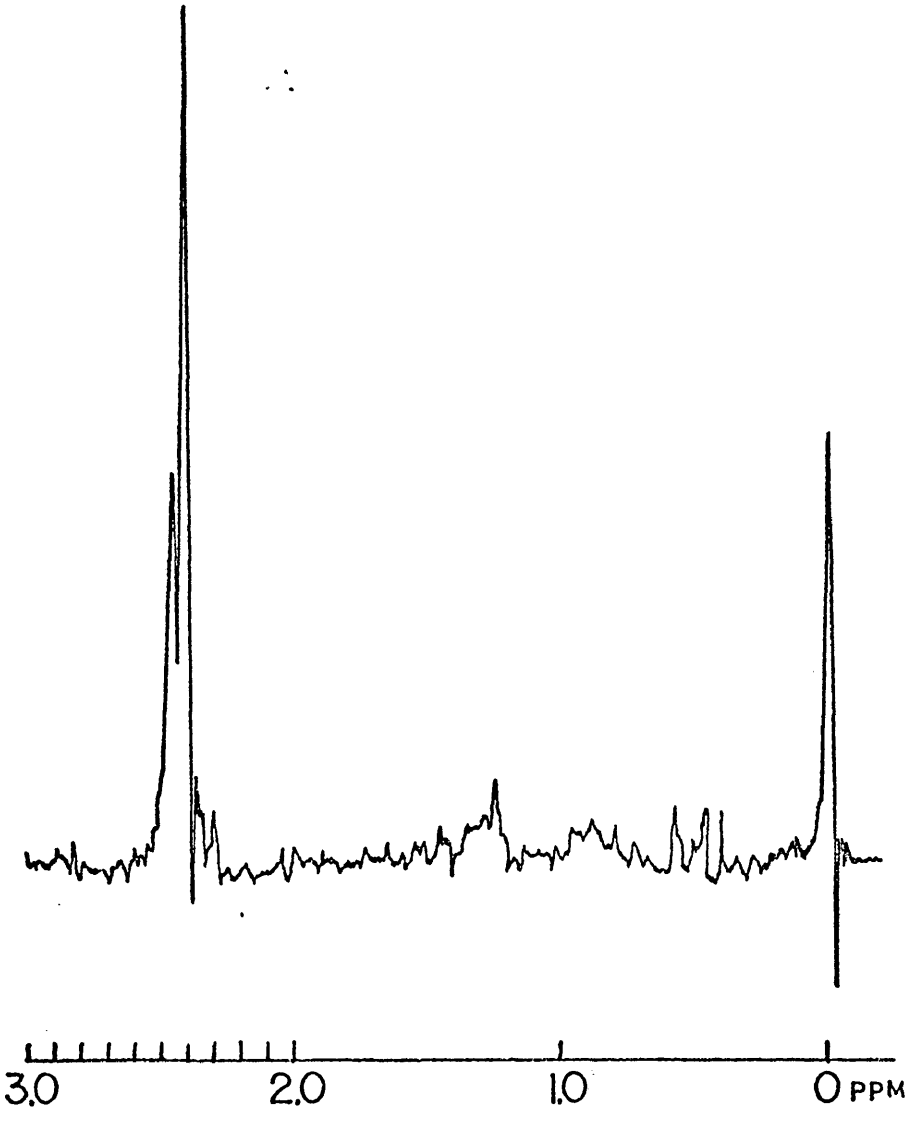


Figure 23

The methyl proton resonances observed in the nmr spectrum of dichlorobis(3-cyanoacetylacetonato)zirconium(IV)

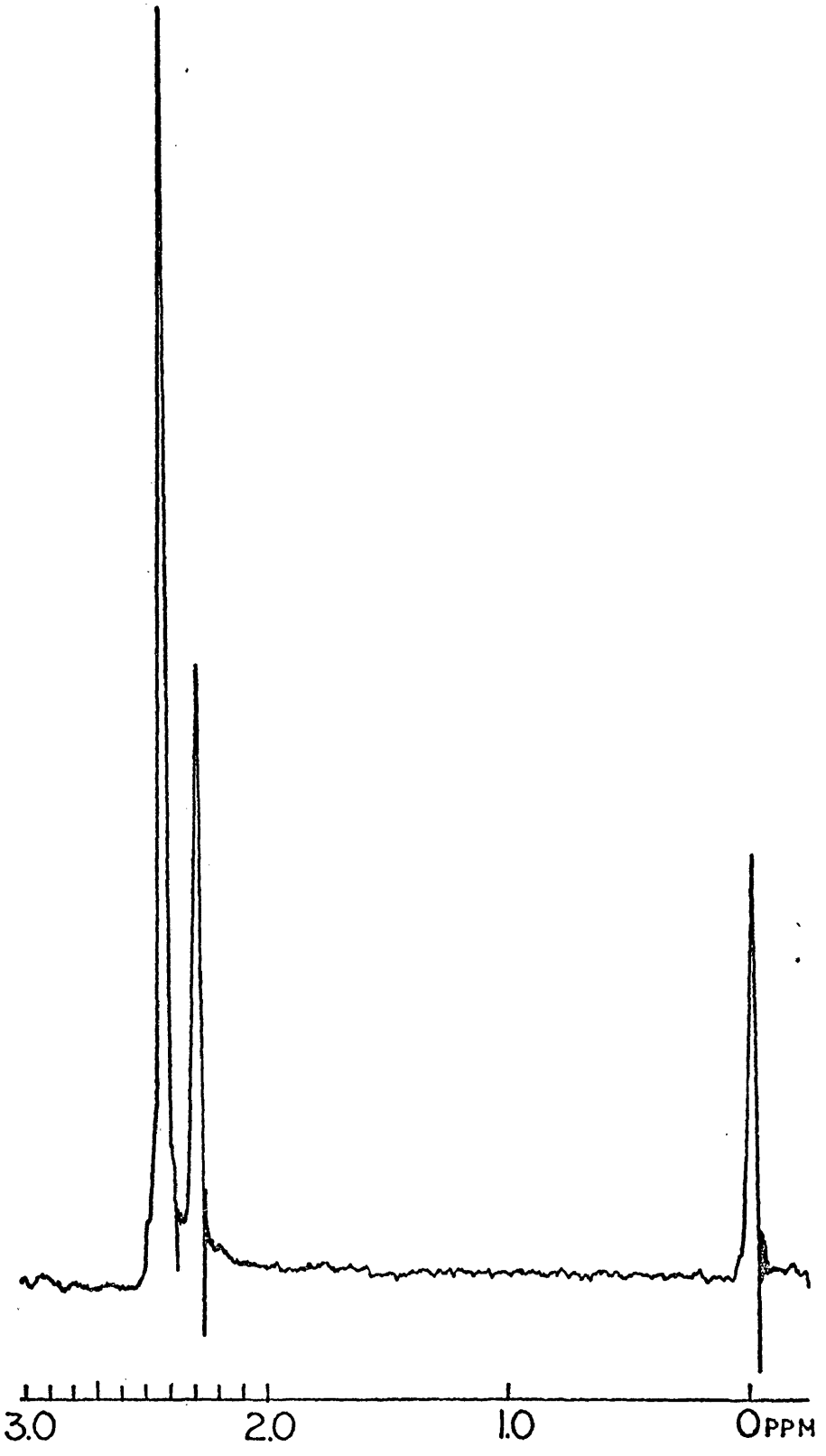


Figure 24

The methyl proton resonances observed in the nmr spectrum of chlorotris(3-cyanoacetylacetonato)zirconium(IV)

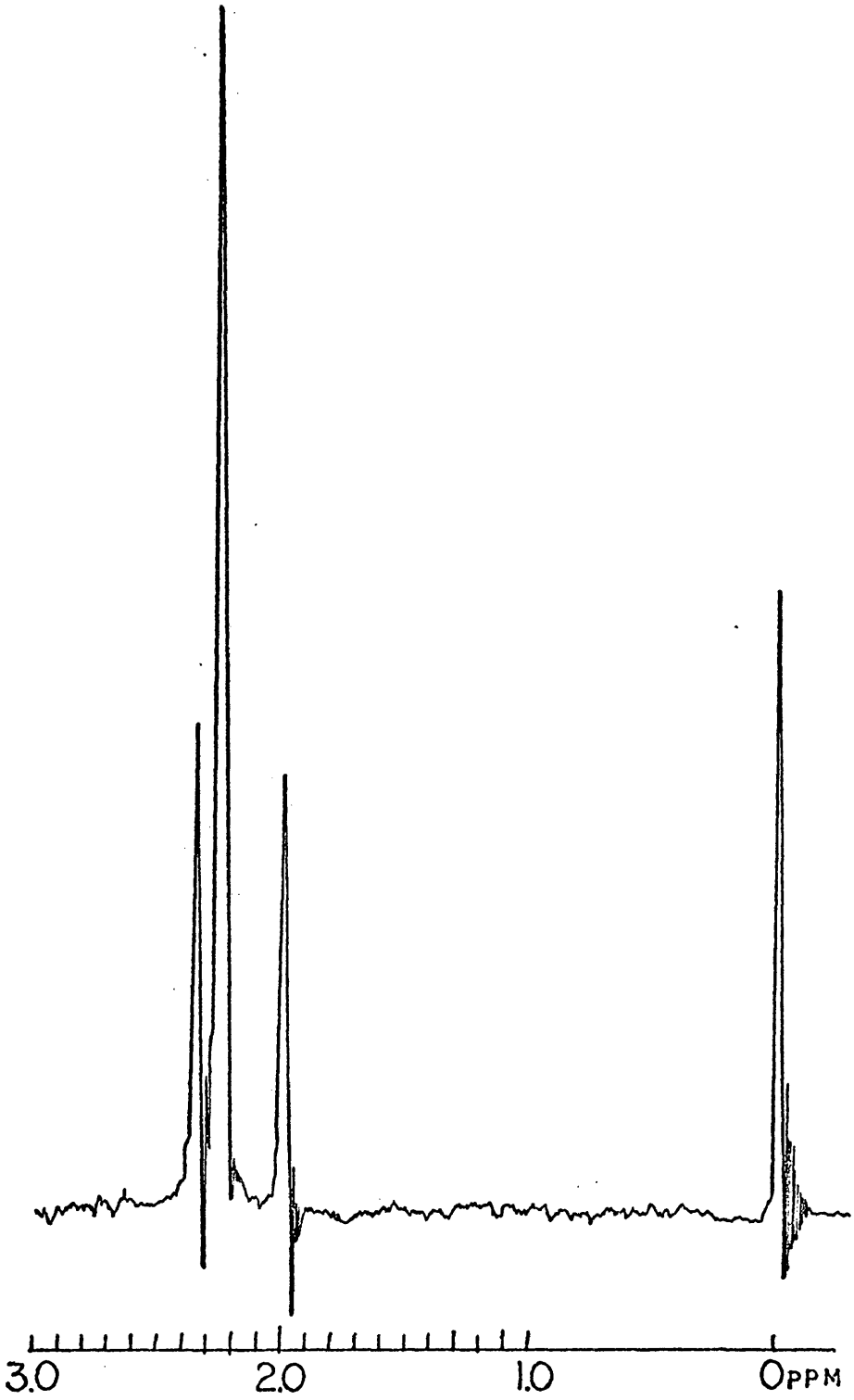


Figure 25
The methyl proton resonances observed in the nmr spectrum of pentahaptocyclopentadienyltris(3-cyanoacetylacetonato)-zirconium(IV)

Figure 26

The methyl proton resonance observed in the nmr spectrum of tetrakis(3-cyanoacetylacetonato)zirconium(IV)

TABLE 7

Proton chemical shift data for zirconium β-diketonate complexes

Compound	$\delta(-CH_3)$[a]	
	L=3-cyanoacetylacetonate	L=acetylacetonate
LH	-2.42	-2.04[28]
$ZrCl_2L_2$	-2.47[c], -2.43[b,c]	-2.14[28]
$ZrClL_3$	-2.45, -2.30[b]	-2.06[28]
ZrL_4	-2.31	-1.96[28]
$Zr(C_5H_5)L_3$	-2.34,-2.25,-1.99	-1.97,-1.89,-1.63[31]

[a]Ppm (±0.02) relative to an internal standard of tetramethylsilane. Temperature is 35°. Solvent, except where noted, is $CDCl_3$.

[b]Peaks are thought to be the result of decomposition of the sample forming the next higher substituted compound. See text.

[c]Solvent is CH_2Cl_2.

is provided in the silicon-acetylacetonate system[36]:

$$3SiCl_2(acac)_2 \rightleftharpoons 2SiCl(acac)_3 + SiCl_4 \ .$$

The nmr data obtained for $ZrCl(CAA)_3$ also support this conclusion as will become apparent in the following discussion.

Because nmr spectra of $ZrCl(acac)_3$ obtained at temperatures as low as -130° also exhibit only one sharp methyl resonance peak,[28] one might expect to see only one peak in the methyl region of the spectrum of $ZrCl(CAA)_3$. Again, however, two peaks are observed and a decomposition of the trisubstituted product, $ZrCl(CAA)_3$, is thought to be the reason:

$$4ZrCl(CAA)_3 \rightleftharpoons 3Zr(CAA)_4 + ZrCl_4 \ .$$

Consequently, the upfield peak is assigned to the more highly substituted $Zr(CAA)_4$. (Again, note the correspondence with the chemical shift reported for $Zr(CAA)_4$.) Only the single low field peak is attributed to the methyl protons of $ZrCl(CAA)_3$.

The spectrum of the pentagonal bipyramidal $Zr(C_5H_5)(CAA)_3$ should, according to its symmetry, exhibit four methyl proton resonance peaks. However, at room temperature, methyl sites A and B (see Figure 20) are thought to be rapidly interchanging with the result that only three peaks are observed. This is quite similar to the observations made on the $Zr(C_5H_5)(acac)_3$ spectrum.[30,31]

The tetrasubstituted product, $Zr(CAA)_4$, exhibits a single sharp methyl proton resonance at 35°. This is consistent with the

spectrum reported for $Zr(acac)_4$ which exhibits only one sharp methyl peak even at -130°.[28] Since both compounds are thought to be square antiprismatic structures, only one methyl peak is to be expected, i.e., all of the methyl sites are thought to be symmetry equivalent.

Finally, two new β-diketones have been prepared and characterized: cyanobenzoylacetone (2-cyano-1-phenyl-1,3-butanedione) and cyanodibenzoylmethane (2-cyano-1,3-diphenyl-1,3-propanedione). Both appear to have properties similar to those of 3-cyanoacetylacetone. The C-N stretching frequencies remain at ~2220 cm^{-1}, unaffected by the phenyl substituents. However, their -OH chemical shifts in the nmr spectrum are increased to 17.44 ppm and 18.03 ppm, respectively, compared to 16.59 ppm for 3-cyanoacetylacetone and 15.25 ppm for acetylacetone.[7] These increases may be due to increases in the strength of the intramolecular hydrogen bond. Like 3-cyanoacetylacetone, these new compounds are white crystalline solids, though significantly higher melting.

REFERENCES

1. Traube, W. Ber., 31, 2944 (1898).

2. Fackler, J. P. J. Chem. Soc., 1957 (1962).

3. Cox, M., Lewis, J., and Nyholm, R. S. J. Chem. Soc., 2840 (1965).

4. Thompson, D. W., Barrett, P. B., Lefelhocz, J. P., and Lock, G. A. J. Coord. Chem., 3, 119 (1973).

5. Wierzchowski, K. L., and Shugar, D. Photochem. Photobiol., 2, 377 (1963).

6. Wierzchowski, K. L., and Shugar, D. Spectrochim. Acta., 21, 931 (1965).

7. Tanaka, M., Shono, T., and Shinra, K. Bull. Chem. Soc. Jap., 42, 3190 (1969).

8. Yoshida, Z., Ogoshi, H., and Tokumitsu, T. Tetrahedron, 26, 5691 (1970).

9. Wierzchowski, K. L., and Shugar, D. Spectrochim. Acta., 21, 943 (1965).

10. Rasmussen, R. S., Tunnicliff, D. D., and Brattain, R. R. J. Am. Chem. Soc., 71, 1068 (1949).

11. Fay, R. C., and Pinnavaia, T. J. Inorg. Chem., 7, 508 (1968).

12. Cotton, F. A., and Wilkinson, G. Advanced Inorganic Chemistry, 3rd ed., Interscience Publishers, New York, 1972, p. 722.

13. Chaigneau, M. Compt. Rend., 239, 120 (1954) as cited in D. F. Shriver, Structure and Bonding, 1, 33 (1966).

14. Spielvogel, B. F., Bratton, R. F., and Moreland, C. G. J. Am. Chem. Soc., 94, 8597 (1972).

15. Melmed, K. M., Li, T., Mayerle, J. J., and Lippard, S. J. J. Am. Chem. Soc., 96, 69 (1974).

36. Thompson, D. W., Inorg. Chem., 8, 2015 (1969); and Thompson, D. W., Rosser, R. W., and Barrett, P. B. Inorg. Nucl. Chem. Lett., 7, 931 (1971).

37. Frazer, M. J., and Newton, W. E. Inorg. Chem., 10, 2137 (1971).

38. Morgan, G. T., and Bowen, A. R. J. Chem. Soc., 125, 1252 (1924).

39. Chattoraj, S. C., Lynch, C. T., and Mazdiyasni, K. S. Inorg. Chem., 7, 2501 (1968).

40. Coever, J., and Curran, C. J. Am. Chem. Soc., 80, 3522 (1958).

41. Brown, T. L., and Kubota, M. J. Am. Chem. Soc., 83, 4175 (1961).

42. Cotton, F. A., and Wilkinson, G. Advanced Inorganic Chemistry, p. 927.

43. Hoard, J. L., and Silverton, J. V. Inorg. Chem., 2, 235 (1963); and Hoard, J. L., and Silverton, J. V., Inorg. Chem., 2, 243 (1963).

16. Bither, T. A., Knoth, W. H., Lindsey, R. V., Jr., and Sharkey, W. H. J. Am. Chem. Soc., 80, 4151 (1958); and Menzer, W. Angew. Chem., 70, 656 (1958) as cited in D. F. Shriver, Structure and Bonding, 1, 33 (1966).

17. Shriver, D. F. Structure and Bonding, 1, 33 (1966).

18. Stocco, F., Stocco, G. C., Scovell, W. M., and Tobias, R. S. Inorg. Chem., 10, 2639 (1971).

19. Buraway, A., Gibson, C. S., and Holt, S. J. Chem. Soc., 1024 (1935).

20. Phillips, R. F., and Powell, H. M. Proc. Roy. Soc., Ser. A, 173, 147 (1939) as cited in F. Stocco, G. C. Stocco, W. M. Scovell, and R. S. Tobias, Inorg. Chem., 10, 2639 (1971).

21. Jain, S. C. J. Inorg. Nucl. Chem., 35, 505 (1973).

22. Walton, R. A. Q. Rev. Chem. Soc., 19, 126 (1965).

23. Jain, S . C., and Rivest, R. Canad. J. Chem., 41, 2130 (1963).

24. Kubota, M., and Schulze, S. R. Inorg. Chem., 3, 853 (1963).

25. Farona, M. F., and Kraus, K. F. Inorg. Chem., 9, 1700 (1970).

26. Thompson, D. W. Structure and Bonding, 9, 27 (1971).

27. Roof, R. B. Acta. Cryst., 9, 78 (1956) as cited in D. W. Thompson, Structure and Bonding, 9, 27 (1971).

28. Pinnavaia, T. J., and Fay, R. C. Inorg. Chem., 7, 502 (1968).

29. Cox, M., Lewis, J., and Nyholm, R. S. J. Chem. Soc., 6113 (1964).

30. Pinnavaia, T. J., Howe, J. J., and Teets, R. E. Inorg. Chem., 13, 1074 (1974).

31. Howe, J. J., and Pinnavaia, T. J., in print.

32. Kontes Glass Company. Vineland, New Jersey 08360.

33. Shriver, D. F. The Manipulation of Air Sensitive Compounds, McGraw-Hill, Inc., New York, 1969.

34. Vacuum Atmospheres Corp. Los Angeles, California 91605.

35. Foll, G. E. Imperial Chemical Industries Ltd., British patent 1,040,383 (1966).

CHAPTER IV

CONCLUSIONS

$ZrCl_2(CAA)_2$, $ZrCl_2(CNbzac)_2$, $ZrCl(CAA)_3$, and $Zr(C_5H_5)(CAA)_3$ are moisture-sensitive compounds, while $Zr(CAA)_4$ is quite unaffected by water. Infrared spectra are consistent with $Zr(C_5H_5)(CAA)_3$ and $Zr(CAA)_4$ being monomeric and $ZrCl_2(CAA)_2$ and $ZrCl(CAA)_3$ being cyclic oligomers. The limited nmr spectral data are consistent with these findings.

Results of the attempts to make the monosubstituted cyclic tetramer, $ZrCl_3(CAA)$, are inconclusive at this time. Also, projections as to the structure of $ZrCl_2(CNbzac)_2$ are not feasible from the limited data obtained so far. Some preparations of zirconium-cyanodibenzoylmethanates have also been unsuccessfully undertaken.

The possibility of synthesizing the monosubstituted tetramer is currently under continuing investigation, as are improved, reproducible preparations for $ZrCl(CAA)_3$. Efforts are also continuing towards the production of crystals of an oligomeric complex suitable for an x-ray crystallographic analysis. The determination of a nondestructive solvent for these compounds may also permit their molecular weights to be calculated.

VITA

George Arbuthnot Lock, Jr.

Born in Baltimore, Maryland, June 26, 1950. Graduated from Hereford Jr.-Sr. High School, June 1968, B.S., College of William and Mary, 1972.

In September 1973, the author entered the College of William and Mary as a graduate student in the Department of Chemistry and became a Candidate for the Degree of Master of Arts in September 1974.